THE CHEMISTRY OF

THE NON-BENZENOID HYDROCARBONS

And Their Simple Derivatives

BY

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First Edition

BOOK DEPARTMENT

The CHEMICAL CATALOG COMPANY, Inc.

ONE MADISON AVENUE, NEW YORK, U. S. A.

1922

Press of
J. J. Little & Ives Company
New York, U. S. A.

PREFACE

The beautiful, interesting, and often facile chemistry of the benzene hydrocarbons has somewhat overshadowed the chemistry of the aliphatic open chain and cyclic non-benzenoid hydrocarbons. Certainly the chemistry of the former series has been much more fully rounded out. Judging from the customary method of treatment accorded them in our textbooks, there is some confusion in the arrangement of subject matter which does not give the student a proper idea of the close relationships and similarity of chemical behavior possessed by all the non-benzenoid hydrocarbons. Mr. Wells, in his "Outline of History," says: "There is a natural tendency in the human mind to exaggerate the differences and resemblances upon which classification is based, to suppose that things called by different names are altogether different, and that things called by the same name are practically identical. This tendency to exaggerate classification produces a thousand evils, . . ." This tendency, which Mr. Wells deplores, is well shown by the use of the term "hydro-aromatic" hydrocarbons and the classification of cyclohexane and its derivatives with benzene. This term is still employed for cyclohexane and its simple derivatives, although its behavior is almost identical with that of normal hexane. The same applies to cyclopentane and its simple derivatives as compared with normal pentane, yet cyclopentane cannot be termed a "hydro-aromatic" hydrocarbon. Cycloheptane, cycloöctane, cyclononane, cyclobutane and cyclopropane should certainly be classed and described together with cyclohexane, as indeed Aschan and a few others have done. The differences in chemical properties between benzenoid ring systems and NON-BENZENOID hydrocarbons are well established, but in spite of the enormous amount of work done, have not yet received adequate explanation.

As regards the aliphatic hydrocarbons proper, these fare very badly in most works on organic chemistry, particularly in the briefer textbooks. Usually, the entirely erroneous statement, or implication, is made that the so-called type reactions given for the first two or three members of the methane series hold good for the higher members. Beyond the fact that all of them may be completely burned to carbon

dioxide and water, such statements are hardly in accord with the known facts. We note that the chemistry of the first five members of the methane series and also the ten carbon atom or terpene group, mostly cyclic hydrocarbons, have been much more extensively and carefully studied than the remainder. Some of the reasons for this are fairly apparent. Thus, the essential oils afford a convenient source of substances of the terpene group which may generally be isolated easily in a state of purity. The natural fatty glycerides or other convenient sources readily yield a limited number of fatty acids, nearly all of them normal, i. e., acids of one, two, three, four, five, six, eight, ten, twelve, fourteen, sixteen, eighteen, and twenty-four carbon atoms. Research in many of these special fields has accordingly been greatly facilitated by the availability of suitable material and has often been much stimulated by an intimate relation to industry.

It may also be pointed out that while in the aromatic series a rich variety of raw materials may easily be isolated or prepared, crystalline derivatives are almost the rule, permitting easy purification, identification, and manipulation in small quantities; that substitution reactions are usually capable of control to form chiefly one product or a very limited number of products or isomers; but in the aliphatic series this is not the case. Petroleums probably contain all of the normal paraffine hydrocarbons up to $C_{26}H_{54}$ and perhaps farther in the series, and perhaps hundreds of naphthenes which are for the most part yet unknown. Not only is it at present impossible to isolate pure individual substances from this complex raw material, but few methods of synthesis applicable to the higher members of the aliphatic series or the more complex naphthenes have been developed.

The reader seeking only material of industrial interest may object to the inclusion of much subject matter which is solely of theoretical interest and the searcher who scorns industrial processes will find much in the present volume that is unorthodox. The author desires to make no apology for the inclusion of both classes of subject matter; the description of any special subject of science should be *systematic* if we are to retain our conception of science as classified knowledge, and the author does not feel that descriptions of industrial processes and references to patent literature detract from the value of the compilation, considered as a scientific monograph. In a treatise of purely industrial purpose the checker-board plan, in which economic value determines exclusion or inclusion of subject matter, may perhaps be justified, but the author believes that the best results will be obtained by broader

scientific treatment of industrial subjects. The author is well aware that patent literature, in spite of oaths and notaries' seals, is not bound by the same standards of truth that govern the publication of purely scientific papers and has accordingly treated such matter critically and with caution.

The mechanical art and engineering of petroleum refining has been perfected to a degree which, measured by profit and general utility, deserves commendation, but it is a development which has been very little dependent upon chemical knowledge. More thorough knowledge of the chemistry of the non-benzenoid hydrocarbons will surely result in better and less wasteful methods of refining and may lead to the conversion of petroleum hydrocarbons into other useful products by chemical methods. In the present state of our knowledge, it would be rash to prophesy what may be accomplished in this direction; but before much work of this kind can be done, *a great deal of painstaking, systematic research in the field of the non-benzenoid hydrocarbons must be carried out which may never be utilized directly in an industrial process.* The writer does not urge research in this field solely on the ground of the utility of the possible results. Those who attempt to justify scientific research by financial returns do not always have a very strong case, and to attempt to balance any particular industry upon the point of an original scientific discovery is to leave out of account the contributions of a host of other people, which the scientist seldom appreciates. Such arguments convince nobody and often arouse the resentment of engineers and business men and others who know better. The upbuilding of a great mass of information and generalizations, new experimental methods and new substances, in the field of the non-benzenoid hydrocarbons, will enable industry to select certain bits of knowledge suited to further progress and our everyday welfare. Every original investigator making real contributions to the fabric of knowledge is thus a contributor to the common weal. This, while not the sole justification of research, is the correct form of the argument of the utility of scientific investigation.

This point of view has a very direct bearing on the question of research in the field of the non-benzenoid hydrocarbons. The petroleum, rubber, turpentine and essential oil industries stand in need of further systematic theoretical research in this field of chemistry. Work along broad lines, involving the work of a great many investigators for a great many years, is required. American chemists have heretofore played a singularly insignificant part in this field of research and to

realize this it is only necessary to mention the names of Wallach, Sir William H. Perkin, Jr., Semmler, Engler, Grignard, Sabatier and the Russian group, Ipatiev, Kishner, Markownikow, Wagner, Konowalow, Zelinsky, Aschan, Bredt, Ostromuislenski, Lebedev, Gustavson, Charitschkov, and others. All of these men have exercised their influence in universities or technical schools, and the inference may accordingly be drawn that we must look to our American universities, rather than to the petroleum or other industrial interests, to initiate and carry on such research in America. And if the American petroleum industries second their efforts, as the Nobel Brothers have done in Russia, a vast amount of work of permanent scientific and potential industrial value can be done.

The present monograph is not a catalog of all the hydrocarbons which might be described. The writer has endeavored to show the close relationships which hold generally throughout the chemistry of the non-benzenoid hydrocarbons and, on the other hand, to point out that the chemical behavior of the more complex hydrocarbons of the paraffine series and the alicyclic hydrocarbons cannot be assumed from the chemical behavior of a few of the simpler hydrocarbons. The chemistry of the ethylene bond is emphasized because of its great importance and because most of our knowledge of its behavior under different circumstances and influences is empirical.

Much important work has been done since the appearance about twenty years ago of Aschan's "Alicyclische Verbindungen" and Semmler's admirable volumes on the terpenes and this work has been briefly reviewed and the attempt has been made to treat it in such a way that will be helpful in wider fields of organic research.

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Chapter I. The Paraffines

In any systematic treatment of the non-benzenoid hydrocarbons, it is difficult to subdivide the subject matter into divisions or chapters, which do not unduly emphasize minor class differences. Thus cyclohexane is not ordinarily considered as a *paraffine* or saturated hydrocarbon although its chemical behavior might very properly place it in this class. On the other hand, the cyclopropane ring frequently exhibits properties of unsaturation which are nearly identical with those characteristic of the ethylene bond. However, since a discussion of the hydrocarbons of the series C_nH_{2n+2} may rationally serve as a ground work, this series will be considered first.

Occurrence of the Paraffines.

From the economic standpoint by far the most important natural sources of the paraffine hydrocarbons are *natural gas*[1] and *petroleum.* The industrial utilization of natural gas has been practically limited to the United States, although the Chinese may claim priority as regards its first industrial use since old Chinese writings describe its collection from shallow dug wells, piping through tubes of bamboo and burning for the evaporation of brine.

Since practically all the natural gas produced in the United States is consumed as fuel or burned for the production of carbon black, very little attention has been paid to its chemical composition. In rare instances natural gas contains as much as 95 per cent methane but an average gas contains about 85 per cent methane, 1.0 to 3 per cent nitrogen and 12 to 15 per cent ethane and other paraffines. Unusual geological conditions, but little understood, result in gases containing large percentages of nitrogen, hydrogen sulfide or carbon dioxide. Hydrogen sulfide is normally not a constituent of natural gas but is frequently encountered in gases in the Gulf Coast territory. Nitrogen occurs in the gas of the northern Texas fields to the extent of about 38 per cent and it is of interest to note that this gas also contains helium

[1] In 1917 the consumption of natural gas in the United States was 795 billion cubic feet. (Northrop in Westcotts' "Handbook of Natural Gas," p. 106.)

in amounts sufficient for its extraction on a large scale for filling dirigible balloons. The composition of natural gas is usually reported in terms of methane and ethane, these percentages being derived by calculation from the results of combustion in an explosion pipette. That hydrogen does not occur in natural gas is now generally accepted, Philipps [2] having shown that the early analyses in which hydrogen was reported, were faulty. Typical analyses reported by Burrell and Oberfell [3] are as follows:

TYPICAL ANALYSES OF NATURAL GAS.

Source of Gas	CH_4 %	C_2H_6 %	CO_2 %	N_2 %	O_2 %	B.T.U. per cu. ft. (760 mm. 0°C.)
Texarkana, Ark.	96	0.0	0.8	3.2	0.0	1,022
Noblesville, Ind.	86.8	6.2	0.8	6.2	0.0	1,040
Leavenworth, Kan.......	91.3	4.5	0.8	3.4	0.0	1,066
Erie, N. Y.	79.9	15.2	0.0	4.9	0.0	1,134
Columbus, O.	80.4	18.1	0.0	1.5	0.0	1,193
Guthrie, Okla.	69.4	20.6	0.1	9.9	0.0	1,062
Muskogee, Okla.	92.1	4.1	0.4	3.4	0.0	1,057
Pawhuska, Okla.	66.5	20.7	0.3	12.5	0.0	1,093
Fort Worth, Tex.[4].......	51.3	10.4	0.1	38.2	0.0	740
Bow Island, Canada [4] ...	87.6	0.9	..	11.2	...	....

The percentages of methane, ethane, propane and higher methane homologues can be determined accurately by fractional distillation at low temperatures.[5] Thus a sample of natural gas supplied to the city of Pittsburgh in 1915 was shown to have the following composition:

Methane	84.7	per	cent.
Ethane	9.4	"	"
Propane	3.0	"	"
Butane and other hydrocarbons................	1.3	"	"
Nitrogen	1.6	"	"

In recent years the practice of removing the light gasoline vapors, mostly butane, pentane and hexane, by absorption and compression methods has become almost universal, at least where large gas supplies are available. High pressure gas from new fields contains relatively very little gasoline vapor, the highest yields being obtained from low pressure gas associated with petroleum.[6] The removal of gasoline va-

[2] *Am. Chem. J. 16,* 406 (1894).
[3] U. S. Bur. Mines. Techn. Paper *109*.
[4] This gas in northern Texas contains about 0.9% helium which is being separated at the U. S. Government plant at Petrolia, Texas. The Canadian gas contains 0.33% helium.
[5] Burrell, Seibert & Robertson. U. S. Bur. Mines. Techn. Paper *104* (1915).
[6] The yield of gasoline obtained by absorption methods from so-called dry gas is from 0.5 to 0.75 gallons per 1000 cubic feet. When the initial gas pressure is 300 to 500 pounds per square inch the yield of gasoline by the absorption method is about 0.3 gallon per 1000 cubic feet. The compression method alone is not employed when the gas contains less than 0.75 gallons of gasoline per thousand cubic feet of gas.

pors slightly lowers the fuel value of the gas, normally one gallon of gasoline per 1000 cubic feet lowering the calorific value of the gas about 5 per cent.[7] The yield of carbon black is considerably diminished by the removal of gasoline vapors from the gas. In common practice the average yield of carbon black was about 1 pound per 750 cubic feet when very rich, low pressure gas was employed for this purpose. The behavior of natural gas under pressure is of industrial importance from another standpoint, i. e., the measuring or metering of gas under pressure. Although the gas pressure of new wells in new fields may be as high as 1600 pounds per square inch, it is usually necessary to compress the gas from lower pressures to about 650 pounds per square inch for transmission through long pipe lines. Methane deviates considerably under pressure, from the behavior of a perfect gas and Amagat[8] has shown that at 40 atmospheres it is about 9 per cent more compressible and at 100 atmospheres is 17 per cent more compressible than a perfect gas. Burrell and Robertson[9] have shown that the average natural gas is considerably more compressible than pure methane, at 35.5 atmospheres this deviation amounting to about 15 per cent as compared to the compressibility of a perfect gas.

The fuel value of natural gas is commonly given as 1000 B.T.U. per cubic foot measured at 0°C but owing to the presence of ethane (1719 B.T.U. per cubic foot) and other hydrocarbons, the value 1100 B.T.U. is a better average value. Since in ordinary fuel practice the water formed in the combustion is practically never condensed, the latent heat of evaporation of this water should be deducted to give a *net* heating value.[10]

Ethane, propane and butane may easily be separated from natural gas in conjunction with the removal of gasoline vapors and, as Burrell and Robertson have shown, each of these hydrocarbons may be isolated in a very pure state by fractional distillation at low temperatures. In view of the low cost of the separation of oxygen and nitrogen by liquid air methods, it is certain that pure ethane, propane and butane could be made available in large quantities at very low cost. These hydrocarbons are not now utilized (other than as fuel), but research in the direction of their chemical utilization is in progress.

[7] Dow. U. S. Bur. Mines. Techn. Paper *253* (1920).
[8] Landolt & Börnstein. *Physikalische Tabellen, 1905,* 65.
[9] U. S. Bur. Mines, Techn. Paper *104* (1915).
[10] Richards, "Metallurgical Calculations," Ed. 1918, p. 25, gives the net heating value of 970 B. T. U. for methane, the water formed remaining uncondensed. Cf. Waidner & Mueller, "Industrial Calorimetry," U. S. Bur. Standards, Techn. Paper *36* (1914).

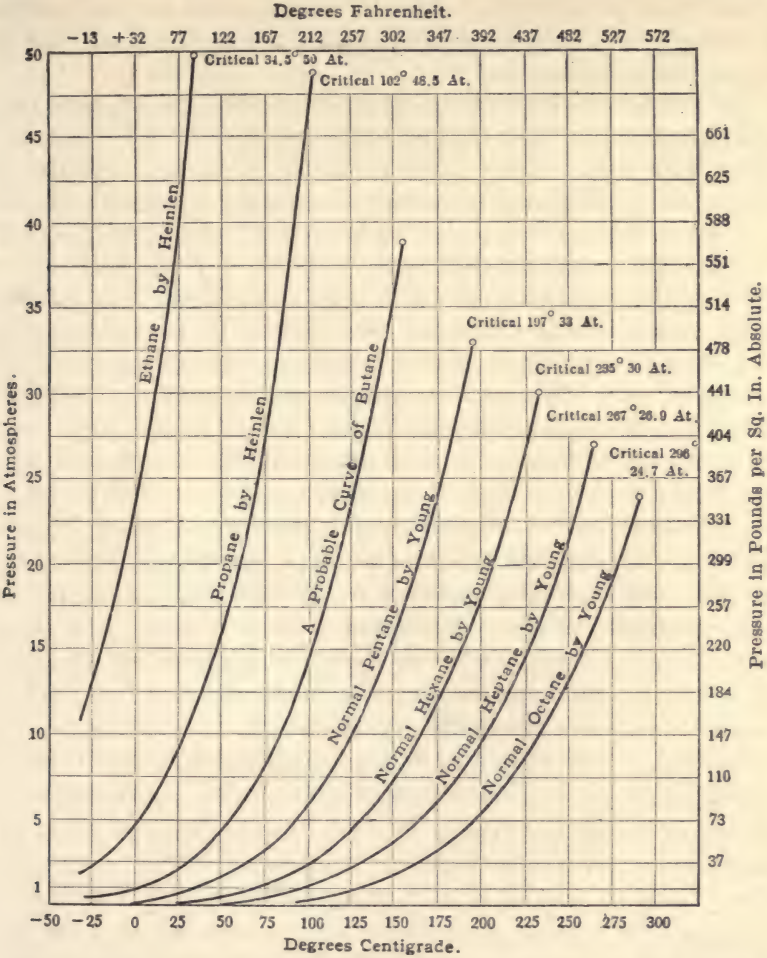
The deviation of ethane, propane and butane from the behavior of a perfect gas is, of course, greater than is the case with methane, and when compressing gas mixtures containing all of these hydrocarbons, as in the separation of gasoline from natural gas by compression, the behavior is the resultant of many factors and the most efficient method of operating a compression plant for the production of gasoline can, at the present time, be determined only by experiment.[11] According to well understood principles, when the pressure on a gas, containing condensable vapors is increased, the partial pressure of the vapor increases until its saturation pressure is reached at which point condensation to liquid begins. Thus if a gas is saturated with pentane vapor at atmospheric pressure, compression to two atmospheres will liquefy one-half of the pentane; if the partial pressure of the pentane is originally one-tenth the saturation pressure, then compression to ten atmospheres will be required to reach the saturation point and this pressure must then be doubled, i.e., to twenty atmospheres, to liquefy one-half the pentane. But when other condensable hydrocarbons are present, these simple relations no longer hold true. The importance of removing the heat resulting by compression is indicated by the accompanying figures showing the vapor pressure curves of the simpler normal paraffine hydrocarbons. See also vapor pressure curves of the simpler paraffines on page 88.

Few *petroleums* consist mainly of hydrocarbons of the paraffine series, but the lighter, low boiling fractions of most petroleums consist of these hydrocarbons almost exclusively. Particularly is this true of light Pennsylvania oil. Since much of the earlier chemical work on petroleum was carried out with distillates of this particular oil, it is often erroneously stated that "American" petroleum consists of paraffines and "Russian petroleum" consists of naphthenes and polynaphthenes of the series C_nH_{2n},C_nH_{2n-2}, etc. Generally it may be said that the petroleums of no two producing regions are the same. Although the petroleum typical of the Pennsylvania field probably contains the largest per cent of paraffines, the higher boiling, viscous fractions of this crude contain but a few per cent of C_nH_{2n+2} hydrocarbons and these are removed by chilling, thus manufacturing the "paraffine wax" of commerce. Lubricating oil derived from Pennsylvania and other petroleums consists chiefly of hydrocarbons of the class C_nH_{2n-2},[12] but their structure is unknown and no pure individual hydrocarbons have

[12] Mabery, *Am. Chem. J.* *1905,* 231.

[11] Anderson, *J. Ind. & Eng. Chem.* *12*, 547 (1920); Dykema, U. S. Bur. Mines. *Bull.* *151* (1918).

been isolated from them. Vaseline isolated from Pennsylvania petroleum, is a mixture of hydrocarbons of the empirical formulae



Vapor pressure curves of the simpler paraffine hydrocarbons. (W. O. Snelling in Hamor and Padgett's "Examination of Petroleum.")

C_nH_{2n-2} and C_nH_{2n-4}. Petroleums from certain American fields contain no paraffines, for examples, Coates[13] has shown that the lighter distillates of the oil from the Jennings, Louisiana, field consist exclusively of cyclic hydrocarbons of the C_nH_{2n} series.

[13] *J. Am. Chem. Soc.* *28,* 384 (1906).

The paraffine wax of commerce consists of a mixture of hydrocarbons of the paraffine series from about $C_{22}H_{46}$ to $C_{26}H_{54}$. The natural waxes of the ceresin type are evidently not normal paraffines but isomeric hydrocarbons probably identical with the amorphous wax of petroleum oils (see below).

The number of hydrocarbons which have been isolated from petroleum is very small. The old procedures, which supplied chemical literature with a formidable array of names, empirical formulae and boiling-points, consisted in carefully fractioning a quantity of petroleum and collecting fractions boiling between narrow limits. Formulae and names were then assigned to these fractions on the basis of combustion analyses and molecular weight determinations. The extremely careful work of Young shows how very difficult the separation of only two hydrocarbons may be when the diffierence in boiling-points is as much as 8°, as in the case of n.pentane and isopentane. Young and Thomas [14] were able to separate n.pentane and isopentane in fairly pure condition only after thirteen fractional distillations through a very efficient dephlegmating column, and Young states that he was not able to isolate pure heptanes from light petroleum ether by fractional distillation. He regards the presence of n.hexane and isohexane in American and Russian petroleums as established, but the presence of other hexanes is open to question. Markownikow was able to isolate cyclohexane and methyl cyclopentane in fairly pure state from Baku oil by a combination of chemical treatments and fractional distillation.[15] In the course of his work, Young showed that benzene and hexane form a constant boiling mixture boiling at 65°–66°. Although the distillation of two closely related hydrocarbons, for example, two members of the series C_nH_{2n+2}, as a constant boiling mixture is very improbable yet it is a possibility. Also owing to the fact that the boiling-points of a series of isomers may extend over a wide range, for example 22° in the case of the hexanes, it is evident that the problem of isolating pure hydrocarbons from petroleum distillates is practically a hopeless one, except in very simple cases as noted above.

Paraffine hydrocarbons are produced in a variety of *biological processes*. The best known example of this method of their production is methane, the name "marsh gas" referring to its formation in bogs where cellulose undergoes anaerobic fermentation. The amylobacteria

[14] *J. Am. Chem. Soc. 71,* 440 (1897).
[15] Aschan, *Ber. 31,* 1801 (1898). Markownikow, *Ann. 301,* 154 (1898); *Ber. 30,* 1532 (1897).

of van Tiegham,[16] evolve methane from cellulose and in this fermentation the other major products are carbon dioxide and the simple fatty acids.[17] Whether small proportions of other gaseous hydrocarbons are simultaneously produced has not been determined. As regards the theory of the biological origin of natural gas and petroleum, the formation of methane from buried cellulose material is capable of experimental duplication but this cannot yet be said of the higher homologues.

Normal heptane has been obtained from the "petroleum nuts" *Pittosporum resiniferum* of the Philippines,[18] from the oleoresin of *Pinus sabiniana* and the wood turpentine of *Pinus jeffreyi*.[19] The higher paraffines occur in small quantity in many essential oils. Commercial rose oil contains sufficient paraffine or "stearoptene" to separate in large crystals, on chilling. This crude stearoptene has been separated into paraffines melting at 22° and 40° to 41°. Heptacosane $C_{27}H_{56}$ and hentriacontane $C_{31}H_{64}$ occur in bees' wax[20] and the latter hydrocarbon also occurs in the resin of tobacco and the leaves of *Gymnema sylvestre, Olea europæa* or the European olive, an African vine *Morinda longiflora* and *Lippia scaberrina*.[21] According to Meyer and Soyka [*Monatshefte, 34,* 1159 (1913)], candelilla wax, used in making phonograph records, contains about 74 to 76 per cent of do-triacontane, $C_{32}H_{66}$. Small quantities of crystalline paraffine wax also occur in certain eucalyptus oils, e. g., *Eucalyptus paludosa* and *Eucalyptus smithii*.[22] Pentatriacontane $C_{35}H_{72}$ melting at 74.5°–75° occurs in the leaves of *Eridictyon californicum*.[23] Pentacontane, $C_{50}H_{102}$, has been found in Lancashire coal. Altogether several tons of dark colored wax were found which after purification and decolorizing melted at 92.7°–93° and boiled at 420°–422° under 15 mm. pressure. This hydrocarbon is the highest homologue of the paraffine series which has been found occuring naturally.[24]

The Character and Probable Mode of Origin of Petroleums.

The development of the petroleum industry had its beginnings almost coincident with the very rapid development of organic chem-

[16] *Compt. rend. 88,* 205 (1879).
[17] Lafar: Tech. Mykologie. Vol. III. 260 (1906).
[18] Bacon, *Philip J. Sci. 4,* 115 (1909).
[19] Schorger, *J. Ind. & Eng. Chem.* 7, 24 (1915).
[20] Schwalb, *Ann. 235,* 110 (1886).
[21] Power & Tutin, *J. Chem. Soc. 91,* 1916 (1907); *93,* 874 (1908).
[22] Smith, *J. Chem. Abs. 106,* 399 (1914).
[23] Power & Tutin, *J. Chem. Soc. Abs. 90,* 885 (1906).
[24] Sinnatt & Barash, *Inst. Min. Eng. 1919,* Nov. 11.

istry. The petroleum industry was largely an American development but extensive research in organic chemistry was for long carried out almost exclusively in Europe, which is one reason for the comparative neglect of petroleum research. Also during these earlier years few American chemists had the facilities and time at their disposal necessary for research. Most American chemists of that period were analytical chemists, with the result that the earlier investigations of petroleum consisted in laboriously fractioning petroleum distillates and christening the various fractions normal undecane, normal dodecane, etc., etc. With the exception of the notable pioneer work of Mabery very little work of permanent value was done on petroleum in America during this long period.

Young demonstrated [26] the presence of n.pentane and isopentane in petroleum, also the presence of n.hexane and isohexane and n.heptane and isoheptane, but considered the presence of isomeric hexanes and heptanes as probable but not proven. The presence of cyclo-hexane, methyl-cyclopentane [27] and a limited number of homologues has been proven in the case of light naphtha from Baku oil. The isolation of a fraction having a constant boiling-point is not necessarily indicative of a pure single hydrocarbon. Two isomers, or two totally different hydrocarbons may have practically identical boiling-points.[28] Five of the known octanes boil within the range 114°–118°. Constant boiling mixtures are also known, the separate constituents of which may have quite different boiling-points. For example, pure n.hexane boils at 68.95° and benzene at 80.2°, but a mixture of the two containing 10 per cent benzene boils at 69° and a mixture containing 27.3 per cent benzene at 69.5°. This behavior of benzene and hexane explains the fact that on nitrating petroleum fractions containing benzene, the fraction yielding the most dinitrobenzene is that boiling at 60°–65°, not that boiling at 75° to 85°. For a similar reason the fraction 90°–100° contains more toluene, when this is a minor constituent, than the fraction distilling at 105°–115°.

All petroleums which contain paraffine hydrocarbons as the chief constituents of their *lighter* fractions, as the Pennsylvania, Mid-Continent, and light Texas crudes, show a rapidly increasing per cent of naphthenes as the boiling-point rises with successive fractions. In the light lubricating fractions the paraffine hydrocarbons, series CnH_{2n+2}, seldom exceeds three per cent and after their removal by chilling, re-

[26] *J. Chem. Soc.* 73, 907 (1898).
[27] Young, *loc. cit.*; Markownikow, *Ber.* 30, 1222 (1897).
[28] Jackson & Young, *J. Chem. Soc.* 73, 926 (1898).

sulting in the paraffine wax of commerce, the lubricating oil remaining is practically free from hydrocarbons of this class. Paraffine wax of commerce, melting ordinarily from 48° to 62° C, consists chiefly of a mixture of hydrocarbons of 23 to 28 carbon atoms. The melting-points and boiling-points of some of the definitely known paraffine hydrocarbons are given in the following table:

Boiling-Points of Hydrocarbons of the Paraffine Series.

Formula	*Name*	*Boiling-Point °C.*
C_4H_{10}	n. butane	— 0.1
"	isobutane	— 10.5
C_5H_{12}	n. pentane	+ 36.3
"	isopentane	27.95
"	tetramethyl-methane	9.5
C_6H_{14}	n. hexane	68.95
"	2 methyl pentane	62.
"	3 methyl pentane	64.
"	2.2 dimethyl butane	49.6 -49.7
"	2.3 " "	58.08
C_7H_{14}	n. heptane	98.2 -98.5
"	2 methyl hexane	89.9 -90.4
"	3 " "	90. -92.
"	trimethyl methane	95. -98.
"	2.2 dimethyl pentane	78.
"	2.4 " "	83. -84.
"	3.3 " "	86. -87.
C_8H_{18}	n. octane	125.8
"	2 methyl heptane	116.
"	3 " "	117.6

Melting-Points and Boiling-Points of Hydrocarbons of the Paraffine Series.

Formula	*Name*	*Boiling-Point °C*	*Melting-Point °C*
C_8H_{18}	4 methyl heptane	118.	
"	2.4 dimethyl hexane	109.8–110.	
"	2.5 " "	109.2	
"	3.4 " "	116. –116.2	
"	diethyl-isopropyl methane	114.	
"	2.2.3.3.tetramethyl butane	106. –107.	+ 103.
C_9H_{20}	n.nonane	149.5	— 51.
"	3 methyl octane	142.4–143.4	
"	4 ethyl heptane	138. –139.	
"	2.5 dimethyl heptane	133. –137.	
"	2.6 " "	132.	
$C_{10}H_{22}$	n.decane	173.	—32.
"	2.6 dimethyl octane	156.5–158.	
"	2.7 " "	159.6	
"	3.6 " "	159.8–160.8	
$C_{11}H_{24}$	n.undecane	194.5	— 26.5
$C_{12}H_{26}$	n.dodecane	214.5	— 12.
"	2.4.5.7 tetramethyl octane	208. –210.	
$C_{13}H_{28}$	n.tridecane	234	— 6.2
$C_{14}H_{30}$	n.tetradecane	252.5	+ 5.5
$C_{15}H_{32}$	n.pentadecane	270.5	+ 10.
$C_{16}H_{34}$	n.hexadecane	287.5	+ 19. –20.
"	7.8 dimethyl tetradecane	263. –265.	below — 30°

MELTING-POINTS AND BOILING-POINTS OF HYDROCARBONS OF THE PARAFFINE SERIES.

Formula	*Name*	*Boiling-Point °C*	*Melting-Point °C*
$C_{17}H_{36}$	n.heptadecane	303.	+ 22.5
$C_{18}H_{38}$	n.octadecane	317.	28.
$C_{19}H_{40}$	n.nonadecane	330.	32.
$C_{20}H_{42}$	n.eikosane	205. (15mm.)	36.7
$C_{21}H_{44}$	n.heneikosane	215. (15mm.)	40.4
$C_{22}H_{46}$	n.dokosane	224.5(15mm.)	44.4
$C_{23}H_{48}$	n.trikosane	234. (15mm.)	47.7
$C_{24}H_{50}$	n.tetrakosane	240. (15mm.)	51.5
$C_{26}H_{54}$	n.hexakosane	......	56.6

Owing to the fact that paraffine wax does not crystallize readily in well formed crystals, even from crude petroleums which are free from asphaltic matter, until after distillation, it has been supposed that the crystalline paraffine is at least partly derived from a parent substance, "proto-paraffine," which breaks up during distillation and thereby yields the freely crystallizing paraffine wax.[29] Rakuzin [30] has shown that crude petroleums contain soft, medium and hard paraffines of crystalline structure. Marcusson [31] slowly distilled ceresine thereby decomposing it to a mixture of well crystallized paraffines and liquid hydrocarbons. The substance known to the refiners as amorphous wax and which gives much trouble to the wax manufacturer, may possibly be ordinary paraffine, whose crystallization is interfered with by colloids, substances capable of gelatinizing on chilling or may in fact consist of paraffine derivatives, "proto-paraffines," for example, naphthenes having very long paraffine side chains which on pyrolysis yield crystalline paraffine wax and an unsaturated naphthene or its polymers. A better method of separating or destroying amorphous wax is a problem of first importance to the refiners, but the real nature of amorphous wax has not been determined. The most definite information on this point is contained in a recent paper by Marcusson [32] who showed that amorphous wax is probably identical with ceresine and there is considerable evidence that ceresine consists of a mixture of branched chain or *iso*paraffines, a hypothesis first put forward by Zaloziecki.[33] Heretofore ceresine has generally been regarded as a mixture of the higher normal paraffine homologues. Marcusson compared the physical and chemical properties of a crystalline paraffine and a refined natural ceresine of practically identical melting points.

[29] Zaloziecki, *Z. f. angew. Chem. 1888,* 126.
[30] *J. Russ. Phys.-Chem. Soc. 1914,* 1544; *J. Chem. Soc. Abs. 106,* 489 (1914).
[31] *Chem. Ztg. 1915,* 581, 613.
[32] *Chem. Ztg. 1915,* 613.
[33] *Z. angew. Chem. 1888,* 126.

	Paraffine	*Ceresine*
Melting-point	56.5° –60.5°	57.5° –60.1°
Solidifying-point	59.2°	59°
Sp. Gr. at 15°	0.885	0.917
Sp. Gr. at 60°	0.781	0.798
Mol. Wt.	330.	420.

Paraffine is harder than ceresine in penetration tests, is markedly more soluble and is less viscous than ceresine at 70°. Paraffine is only slightly attacked by fuming sulfuric acid, 33% SO_3, at ordinary temperatures, but ceresine is energetically attacked. The action of nitric acid is also more energetic on ceresine. On dissolving paraffine in hot mineral oil and then cooling, the paraffine crystallizes out but with ceresine, under the same conditions, a vaseline-like deposit is obtained. Marcusson has examined the distillation products of ceresine and the oily product consists of a mixture of saturated hydrocarbons and olefines of low molecular weight. No evidence of the presence of naphthenes was obtained.

The formation of branched chain hydrocarbons or so-called *iso*-paraffines may possibly be explained by the decomposition of montan wax, which as shown by Meyer and Brod [34] consists chiefly of an acid, $C_{28}H_{56}O_2$, and a solid alcoholic wax. This acid of montan wax is not a normal chain fatty acid but a branched chain compound.

Paraffine is formed during the distillation of asphalt base oils by the decomposition of the asphaltic matter. This is in accord with the observation that large amounts of crystalline paraffine are contained in shale oil, the wax not being present as such in the original shale but formed by the decomposition of the complex kerogen of the shale; also the distillate obtained by the low temperature distillation of coals rich in volatile matter contains crystalline paraffine, which is not present as such in the original coal.

In addition to the problem of separating simple mixtures of hydrocarbons by fractional distillation and the separation of paraffine wax by chilling and crystallizing, it should be noted that other special methods must be resorted to, to isolate substances of a particular class from a particular petroleum. Petroleums contain varying proportions of the following classes of substances, all of which are very imperfectly known chemically:

(1) Paraffine hydrocarbons, liquid and solid, series C_nH_{2n+2}.
(2) Saturated monocyclic or napththene hydrocarbons, empirical formula C_nH_{2n}.
(3) Saturated polycyclic hydrocarbons, empirical formulae. C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, etc.

[34] Monatshefte, *1913*, 1153.

(4) Benzenoid hydrocarbons and derivatives.
(5) Unsaturated hydrocarbons. (Present in distillates but probably not present in most crude petroleums.)
(6) Asphaltic matter.
(7) Sulfur derivatives.
(8) Nitrogenous substances.
(9) Organic acids ("naphthenic" acids, not of the fatty acid series).
(10) Coloring matter and fluorescent substances (these substances may belong to other classes enumerated above).

The majority of American petroleums yield gasolenes and kerosenes consisting chiefly of paraffine hydrocarbons. All American petroleums which contain large proportions of these lighter distillates, such as the light Appalachian, mid-Continent and northern Texas crudes, yield gasolene and kerosene of this character. Low boiling distillates consisting of *cyclic* hydrocarbons or naphthenes are usually derived from heavier crudes yielding very little of the lighter distillates for example, the heavy California and the Jennings, Louisiana crude from which Coates [35] has isolated dicyclic hydrocarbons $C_{10}H_{18}$ to $C_{13}H_{24}$ and the Russian and Galician oils from which cyclopentane, cyclohexane, and a series of their derivatives has been isolated.[36] The determination of the structure of these naphthenes, coupled with the difficulty of their isolation in a state of purity, is a task as difficult as any in organic chemistry, and it is doubtful if very much light will be thrown on their constitution until it is shown that chemical methods of utilization may lead to the extraction of greater profits, than are now obtained, though it is easily conceivable that the latter result cannot be arrived at without the former.

Beilstein and Kurbatow [37] showed that the more volatile hydrocarbons of Russian petroleum possessed the empirical formula C_nH_{2n}, exhibited none of the reactions of olefines and in their general chemical behavior resembled the hydrocarbons of the methane series. Two hydrocarbons of the formula C_6H_{12}, one [38] boiling at 72° and the other [39] at 80° were isolated. Cyclohexane, prepared by Baeyer, proved identical with the latter hydrocarbon from Russian petroleum and it was then shown that the isomeric hydrocarbon was methyl cyclopentane. Markownikow obtained evidence of the presence of cycloheptane in the fraction boiling at 115°–120° of a Caucasian oil. With the exception of the bicyclic decahydronaphthalene isolated by Ross and Leather [40]

[35] *J. Am. Chem. Soc.* *28*, 384 (1906).
[36] *Ann.* *301*, 154 (1898); *302*, 37 (1898);
[37] *Ber.* *13*, *1818*, 2028 (1880). *307*, 342 (1899).
[38] Kishner, *J. Russ. Phys.-Chem. Soc.* *20*, 118 (1890).
[39] Markownikow, *Ann.* *302*, 1 (1898).
[40] *Analyst* *31*, 284 (1906); This hydrocarbon is now made commercially by the catalytic hydrogenation of naphthalene.

from Borneo petroleum the structure of the higher boiling naphthenes is largely a matter of conjecture.

PHYSICAL PROPERTIES OF SOME SATURATED CYCLIC HYDROCARBONS.

Name	*Empirical Formula*	*Boiling-Point °C*	*Sp. Gr.*
Cyclopropane [41]	C_3H_6	—35.	.....
Cyclobutane [42]	C_4H_8	11. – 12.	$0.7038\frac{0^\circ}{4^\circ}$
Methyl cyclopropane [43]	$C_3H_5CH_3$	4. – 5.	.....
*Cyclopentane [44]	C_5H_{10}	49.	$0.7635\frac{0^\circ}{4^\circ}$
Methyl cyclobutane [45]	$C_4H_7.CH_3$	39. – 42.	.....
1.1 dimethyl cyclopropane [46]	$C_3H_4{<}{CH_3 \atop CH_3}$	21.	.....
*Cyclohexane [47]	C_6H_{12}	81.	$0.7934\frac{0^\circ}{4^\circ}$
*Methyl cyclopentane [48]	$C_5H_9.CH_3$	70. – 71.	.....
Ethyl cyclobutane [49]	$C_4H_7.C_2H_5$	72.2– 72.5	$0.7540\frac{10^\circ}{4^\circ}$
1.2.3. trimethyl cyclopropane [50]	$C_3H_3.(CH_3)_3$	65. – 67.	$0.6946\frac{18^\circ}{4^\circ}$
1.1.2. " " [50]	$C_3H_3.(CH_3)_3$	57. – 59.	$0.6832\frac{19^\circ}{4^\circ}$
Cycloheptane (suberane) [51]	C_7H_{14}	118.	$0.8275\frac{0^\circ}{4^\circ}$
*Methyl cyclohexane [52]	$C_6H_{11}.CH_3$	100. -101.	$0.7662\frac{18^\circ}{4^\circ}$
1.1 dimethyl cyclopentane [53]	$C_5H_8.(CH_3)_2$	88.	$0.7547\frac{20^\circ}{0^\circ}$
1.2 " " [53]	$C_5H_8.(CH_3)_2$	92. – 93.	$0.7581\frac{18^\circ}{0^\circ}$
i-1.3 " " [53]	$C_5H_8.(CH_3)_2$	93.	$0.7410\frac{24^\circ}{4^\circ}$
Cyclo-octane [54]	C_8H_{16}	145.3–146.3 M.-Pt. 11.5	$0.850\ \frac{0^\circ}{4^\circ}$
Ethyl cyclohexane [51, 55]	$C_6H_{11}C_2H_5$	132. –133.	$0.7913\frac{0^\circ}{0^\circ}$
1.1 dimethyl cyclohexane [56]	$C_6H_{10}(CH_3)_2$	120.	.....
1.2 dimethyl cyclohexane [57]	$C_6H_{10}(CH_3)_2$	124.	$0.8002\frac{0^\circ}{0^\circ}$

[41] Ladenburg & Krügel, *Ber.* *32*, 1821 (1899).
[42] Willstätter & Bruce, *Ber.* *40*, 3979 (1907).
[43] Demjanow, *Ber.* *28*, 21 (1895).
[44] Markownikow, *Ann.* *327*, 59 (1903).
[45] Perkin & Colman, *J. Chem. Soc.* *53*, 201 (1888).
[46] Gustavson & Popper, *J. pr. Chem.* (2), *58*, 458 (1898).
[47] Perkin & Freer, *J. Chem. Soc.* *53*, 203 (1895).
[48] Zelinsky & Gutt, *Ber.* *41*, 2431 (1908).
[49] Zelinsky & Zelikow, *Ber.* *34*, 2857 (1901).
[50] Willstätter & Kametaka, *Ber.* *41*, 1480 (1908).
[51] Sabatier & Senderens, *Compt. rend.* *132*, 566 (1901).
[52] Kishner, *Chem. Cent.* *1908*, II, 1860.
[53] Zelinsky & Rudsky, *Ber.* *29*, 405 (1896).
[54] Willstätter & Veraguth, *Ber.* *40*, 968 (1907).
[55] Kursanoff, *Ber.* *32*, 2973 (1899).
[56] Crossley & Renouf, *J. Chem. Soc.* *87*, 1498 (1905).
[57] Sabatier & Mailhe, *Compt. rend.* *141*, 20 (1905).

PHYSICAL PROPERTIES OF SOME SATURATED CYCLIC HYDROCARBONS.

Name	*Empirical Formula*	*Boiling-Point °C*	*Sp. Gr.*
1.3 dimethyl cyclohexane [57]	"	118.	$0.7869\frac{0°}{0°}$
1.4 " " [57]	"	119.	$0.7861\frac{0°}{0°}$
1 methyl-3-ethyl cyclopentane [58]	$C_5H_8<^{CH_3}_{C_2H_5}$	120.5–121.	$0.7669\frac{16°}{4°}$
1.1.2 trimethyl cyclopentane [59]	$C_5H_7(CH_3)_3$	113. –113.5	$0.7847\frac{4°}{4°}$
Cyclononane [60]	....	170. –172.	.....

Aromatic, or benzenoid, hydrocarbons have been found, usually in very subordinate proportions, in all petroleums which have been carefully investigated. The per cent by volume of benzenoid hydrocarbons present, as reported, is often too high particularly when nitration methods have been employed. This error is due to the relative ease with which non-benzenoid hydrocarbons are nitrated. Thus Edeleanu and Gané [61] report a yield of 41% nitro products from gas oil from Pennsylvania oil, a figure obviously far too high to accord with the empirical combustion analysis and well known behavior of this oil to consider this figure as an indication of the proportion of benzene derivatives present. However in the case of the lighter distillates the crystalline nitrated products can often be isolated and positively identified. The presence of benzene has been shown in petroleums of various origins and Mabery [62] had no difficulty in isolating naphthalene from a California oil by fractional distillation, the fraction boiling at 220°–222° finally solidifying in the condenser. According to Jones and Wootton [63] Borneo petroleum contains 6 to 7 per cent hydrocarbons of the naphthalene series. This oil contains mono and dimethyl derivatives of naphthalene. Brooks and Humphrey [64] found small quantities of benzene and toluene in gasolene made by distilling the heavy high boiling residue of Oklahoma oil at about 420°C. and under a pressure of about 100 pounds. Inasmuch as practically no hydrogen is present in the gases formed in the process they suggested that these small percentages of benzene and its simpler homologues were formed as de-

[58] Zelinsky, *Ber. 35,* 2679 (1902).
[59] Crossley & Renouf, *J. Chem. Soc. 89,* 33 (1896).
[60] Zelinsky, *Ber. 40,* 3279 (1907).
[61] *Rev. gen. Petrol. 1910,* 393.
[62] *J. Soc. Chem. Ind. 19,* 52 (1900).
[63] *J. Chem. Soc. 91,* 1146 (1907).
[64] *J. Am. Chem. Soc. 38,* 393 (1916); The formation of benzene and toluene at much higher temperatures, as in the Hall or Rittman process, is an altogether different matter. In this latter process hydrogen is always an important constituent in the evolved gases and it makes little difference what petroleum oil fraction is employed, in fact fairly pure pentane or hexane or paraffine wax will yield substantial quantities of benzenoid hydrocarbon under these conditions. Cf. Egloff & Twomey, *J. Phys. Chem. 20,* 515 (1916); Egloff, *Met. & Chem. Eng. 15,* 692 (1916).

composition products of high boiling benzene derivatives which were present in the original petroleum, rather than by the dehydrogenation of saturated cyclic hydrocarbons.

Petroleums are normally free from olefinic hydrocarbons. Such hydrocarbons are, however, invariably present in petroleum *distillates.* LeBel [65] found amylene and two isomeric hexenes in the light distillate from a petroleum from Pechelbronn, but regarded them as decomposition products formed during distillation of the crude oil. Balbiano and Paolini [66] detected olefines in an American kerosene (by the formation of a precipitate with mercuric acetate), and Mabery and Quayle [67] reported hexenes, heptenes and octenes in a distillate from a Canadian petroleum. But in so far as the presence of olefines in crude petroleum is concerned, a clear demonstration of their presence is lacking, except in the case of a sample examined by Zaloziecki [67] and said to have come from Java. The occurrence of terpene like hydrocarbons has sometimes been reported but Coates has shown that the turpentine-like odor of the Jennings, Louisiana, oil is due to saturated bicyclic hydrocarbons and that this petroleum contains no olefines. The presence of olefines cannot be demonstrated or quantitatively measured by the usual iodine or bromine absorption methods owing to substitution reactions taking place. These methods invariably give too high results in the case of pyrolytic distillates.

The relative ease with which olefines are polymerized by fuller's earth and similar substances may explain the absence of these unsaturated hydrocarbons in petroleums. Until an authentic crude petroleum can by proper experimental methods be shown to contain them, the statement that olefinic hydrocarbons are not present in crude petroleums seems amply justified.

Very little is known regarding the *sulfur compounds* contained in crude petroleums and distillates. The refiner is concerned only with deodorizing the distillates and the chemical character of the sulfur derivatives is of no interest to him. The well known method of Frasch, consisting in the desulfurizing of oil by treatment with copper oxide, was developed particularly for oils from Canada and the Lima-Indiana field and Mabery and Quayle [68] have investigated the sulfur compounds of the Canadian oil and discovered what is apparently a new series of organic compounds of sulfur. By distilling the oil in

[65] *Compt. rend.* *75,* 267 (1872) ; *81,* 967 (1875).
[66] *Chem. Ztg.* *1901,* 932.
[67] *Naphtha,* *1900,* 222.
[68] *Am. Chem. J.* *35,* 404 (1906).

vacuo and treating the distillates with alcoholic mercuric chloride they obtained precipitates of the sulfur compounds which were then decomposed by hydrogen sulfide. In empirical composition these substances are identical with hydrothiophenes (which have not been made synthetically), and Mabery has designated them as thiophanes. They are oxidized by permanganate or chromic acid to sulfones, thick, viscous oils of slight, rather pleasant odors, and they combine with ethyl iodide to form products of the empirical composition $C_nH_{2n}S.C_2H_5I$, the iodine being replaceable by hydroxyl, by means of silver oxide, to give basic substances. The thiophanes are comparatively stable. Mexican petroleums contain as much as 7.5% sulfur but no differentiation between dissolved or suspended free sulfur and combined sulfur has been made. Mexican and many of the Gulf coast oils contain free sulfur [69] and on distillation hydrogen sulfide is evolved. Organic bases such as aniline, pyridine and quinoline, and also ammonia react with many, perhaps all, of the sulfur compounds contained in petroleums, pyridine being said to "catalyse" the evolution of hydrogen sulfide. The desulfurizing of petroleum by heating in the presence of free ammonia, hydrogen sulfide being formed, has been proposed by F. M. Perkin.[70]

By retorting certain shales, distillates rich in sulfur are obtained which may be sulfonated by concentrated sulfuric acid and the product, in the form of water soluble ammonium salts, is the material known in pharmacy and medicine as *"ichthyol,"* so named because the shales in Austria from which the ichthyol oil was first derived are rich in fossil fish remains. The product is a complex mixture of substances, of variable composition and practically nothing is known as to the chemical nature or structure of the sulfur derivatives in the original distillate. Other shales yield similar distillates, for example:

	Per cent				
Oil from shale at,	C.	H.	N.	O.	S.
St. Champ, France [71]	77.3	9.2	0.37	1.14	11.99
Tuscany	69.5	8.7	2.27	11.6	7.79

In preparing ichthyol, the crude distillate is sulfonated by treating with ordinary concentrated sulfuric acid, slightly diluted with water or brine and the unsulfonated oil extracted by petroleum ether and the sulfonic acids, neutralized by ammonia. The commercial product always contains ammonium sulfate on account of the practical impossibility of completely removing the excess sulfuric acid.[72] The crude

[69] Richardson, *J. Soc. Chem. Ind.* *21,* 316 (1902).
[70] *Chem. Trade J.* *50,* 251 (1917).
[71] Demesse & Reaubourg, *Bul. Soc. chim.* *15,* 625 (1914).
[72] Puckner, *Lab. Rep. Am. Med. Assn.* *5,* 110.

oil contains, in addition, to sulfur compounds, phenols and organic acids.[73]

The occurrence of nitrogen bases in petroleum is by no means rare and the percentage of such bases in many crude petroleums is relatively large. Ordinarily the proportion of nitrogen in petroleum does not exceed 1.5 per cent but an Algerian oil is reported as having 2.17 per cent and a Japanese 2.25 per cent. The highest per cent of nitrogen thus far reported is 2.39 per cent, found in a Californian oil. This means that probably 20 per cent of this oil consists of nitrogen bases. Very little is known as to the character of these bases. The separation of definite substances by fractional distillation of the bases recovered from the acid washings of the oil has not been successful. They form precipitates from acid solutions with platinum, palladium, mercuric, cadmium and ferric chlorides, potassium dichromate, ferro and ferricyanides and picric and oxalic acids. By oxidation with alkaline permanganate in alkaline solution the nitrogen is evolved partly as free nitrogen and partly as ammonia. Oxidation by chromic acid has led to no definite results. Decomposition by the method of exhaustive methylation does not appear to have been given a fair trial; ethyl iodide combines with these bases when heated together in a sealed tube. The bases are weakly basic. In 1900 Mabery[74] concluded that the nitrogen bases in California petroleum consisted of a mixture of more or less hydrogenated quinolines. Recently Mabery has returned to the problem and in a recent paper, with L. G. Wesson,[75] has shown that by careful oxidation with potassium permanganate, the various fractions, derived from the crude mixture of bases yield pyridine pentacarboxylic acid and methyl pyridine tetracarboxylic acid. No higher fatty acids were observed among the oxidation products. By oxidizing with chromic acid and subjecting the calcium salts of the acids thus formed to dry distillation, β-methylquinoline is produced. Mabery and Wesson conclude that the organic bases of California petroleum consist mainly of an indefinite mixture of alkylated quinolines or isoquinolenes, the rings containing the nitrogen being completely alkylated by small alkyl groups.

Origin of Petroleum.

The great preponderance of opinion among geologists and chemists is in favor of the theories of the origin of petroleum from organic rather

[73] Scheibler, *Ber.* 48, 1815 (1915).
[74] *J. Soc. Chem. Ind.* 19, 505 (1900).
[75] *J. Am. Chem. Soc.* 42, 1014 (1920).

than inorganic sources. [In view of this fact a discussion of the theories of inorganic origin will be omitted here but good reviews of this phase of the subject are available in many standard works.[76]] A great deal has been written on this theme but experimental evidence is almost altogether lacking. The chief evidence is of an altogether different nature, namely geological and geochemical on the one hand and the general chemical character of petroleums on the other. The question is one that hardly lends itself to direct experimental study.

Both animal and vegetable matter have probably contributed to the formation of petroleums and natural gases and decay of such organic matter appears to be easily adequate to the formation of the quantities of oil and gas which are found buried in the strata. Geologists [77] have called attention to the fact that petroleum is very widely disseminated through many limestone and sandstone strata of enormous thickness and area. Thus it has been estimated that in the limestone of Chicago, which has a thickness of about 35 feet, there are over 7,000,000 barrels of oil in each square mile of this stratum.

The deposits of petroleum at Baku and the surrounding territory are, nearly all, in Tertiary formations, and the menilite shale in which the petroleum occurs is certainly of marine origin. It has been estimated that if the annual deposition of fish remains in these rocks were equivalent to the annual catch in the fisheries of northern Europe, and that only 50 per cent of the oil in these remains were converted into petroleum, a period of about 2500 years would suffice for the entire petroleum accumulations in the Carpathian area. Engler has pointed out that both animal and vegetable remains may have contributed to the formation of petroleum and Kraemer and Spilker [78] have pointed out that certain algae contain droplets of oil in their cells.

Petroleums may be very much altered by filtration through fine sand or other fine material as has been shown experimentally by the work of Day, Gilpin and Kramm and others, the more fluid and volatile hydrocarbons being gradually separated from the more complex and less volatile constituents. This undoubtedly accounts for the character of certain crude petroleums which are very slightly colored and sometimes contain upwards of 30% of gasolene. In the accumulation of such oils in pools, the oil must in many cases have traveled long distances through the porous rock.

[76] Data of Geo-Chemistry by F. W. Clark, Bulletin 695, U. S. Geological Survey, Washington, 1920.

[77] Orton, Ohio Geological Survey, First Annual Report 1870, and Hunt: Chemical and Geological Essays 1875, p. 168.

[78] *Ber.* *35*, 1212 (1901).

Practically all petroleums which have been investigated give distillates which show slight optical activity. Inasmuch as no synthetic process, such as the formation of hydrocarbons from carbides and the like, yields optically active material, the presence of optically active substances in petroleum is considered to be one of the strongest arguments in support of the organic origin of petroleum. Although pure fatty glycerides are not optically active, natural fats and oils contain small quantities of cholesterol, phytosterol, protein decomposition products and the like which are optically active. When oils containing cholesterol or phytosterol are subjected to distillation under pressure the maximum optical activity is observed in the same fractions, with respect to boiling point, as is the case with petroleum distillates.[79]

It is not too much to expect that further study will reveal the chemical history of the formation of petroleum as clearly as the formation of coal is revealed in the series of changes through peat, the lignites, bituminous coals and anthracite. This information will undoubtedly be obtained through a study of superficial or recently buried deposits rather than by experimental work seeking to produce the results by laboratory methods. Phillips observed the anaerobic fermentation of sea weeds in an apparatus which was observed over a period of two and a half years. At first a little methane together with larger quantities of carbon dioxide, hydrogen and nitrogen were evolved but toward the end of the experiment the evolved gas consisted chiefly of methane.

In addition to the geological evidence of the organic origin of petroleum, a wealth of evidence is found in the chemical character of petroleums themselves, particularly the optically active constituents, naphthenic acids, nitrogen and sulfur derivatives.

A great deal of the experimental investigations which have given support to the organic theory have been carried out by Engler and his students.[80] Engler believes that in the anaerobic decay of marine animal remains the fatty oils, being more resistant to putrefactive changes, remain entangled in the marine sediments long after the proteins and other organic constituents have been lost by putrefactive decay. He has shown that when fish oil is heated or distilled under pressure, good yields of a liquid hydrocarbon mixture are obtained, which

[79] Walden, *Chem. Ztg.* **30**, 391, 1155, 1168 (1906); Rakuzin, *8th Int. Cong. Appl. Chem.* **25**, 721; *Ber.* **42**, 1211, 1640, 4675 (1908); Marcosson, *Chem. Ztg.* **32**, 377, 391 (1908); Ubbelohde, *Ber.* **42**, 3242 (1909); **43**, 608 (1910).

[80] *Ber.* **21**, 1816 (1888); **26**, 1449 (1893); **30**, 2365 (1897); *Z. f. angew. Chem.* **1908**, 1585; *Ber.* **42**, 4610, 4613, 4620 (1909); **43**, 388, 954 (1910); *Z. f. angew. Chem.* **1912**, 4.

very greatly resembles crude petroleum in its physical characteristics and chemical composition. Such distillates have a marked green fluorescence and in the lighter fractions, obtained by fractional distillation, n.pentane, n.hexane, n.heptane, n.octane, and nonane were identified. By chilling the fraction boiling above 300° crystalline paraffine, melting-point 49° to 51°, was obtained and also a viscous fraction closely resembling lubricating oil was isolated. These distillates obtained by Engler contained notable percentages of unsaturated hydrocarbons, thus differing from crude petroleum but this difference is readily understood, in view of the experimental demonstration of Gurwitsch [81] that fuller's earth rapidly polymerizes unsaturated hydrocarbons. Thus at ordinary temperatures amylene is 85% polymerized in two days. Engler's distillates contain small quantities of aromatic hydrocarbons, benzene, toluene and xylene being identified by their nitro compounds, these distillates resembling crude petroleums in this respect. Very similar results were obtained by distilling animal and vegetable oils and fats under pressure.

Although the strata in which petroleum oils occur are never found at sufficient depth to be subjected to the temperatures employed by Engler and in most cases have not been subjected to volcanic intrusions, marked folding of the strata or other sources of heat, Engler, nevertheless, supposes that these same destructive changes which he effects by pressure distillation may be effected in Nature at very much lower temperatures during the long course of geologic time. Though little is definitely known in regard to the substances in petroleum which contain oxygen and sulfur, the mere presence of these substances is indicative of an organic rather than an inorganic origin. Mabery has shown that the nitrogenous constituents of California petroleum are hydrogenated quinolines.[82]

Asphaltic matter is undoubtedly formed by oxidation, which process readily explains such deposits as that of Trinidad Island and such a process is closely duplicated in the well-known process of Byerley and Mabery of blowing air through the heavy residuum left in the stills after the more volatile fractions have been distilled from crude petroleums.

As regards sulfur compounds these have been ascribed to the decomposition of organic remains and it is noteworthy that certain oils rich in sulfur are associated with shales containing abundant fossil re-

[81] *J. Russ. Phys.-Chem. Soc.* **47**, 827 (1915); *J. Chem. Soc.* **1915**, I, 933.
[82] *J. Am. Chem. Soc.* **42**, 1014 (1920).

mains of fish. This is particularly true of the Austrian deposit from which the well-known pharmaceutically valuable "ichthyol" is derived. These sulfur compounds, however, *may* have been formed in a very different manner. It is well known, for example, that sulfates can be reduced by organic matter or by anaerobic fermentation with the formation of sulfur. Sulfur in very large masses is often found associated with petroleum in the American Gulf Coast region and its formation is perhaps best accounted for in this manner. It is also well known that free sulfur reacts with hydrocarbons with relative ease. The direct addition of sulfur to unsaturated hydrocarbons has been shown by Erdmann. Reaction with saturated hydrocarbons, paraffine for example, can be effected at very moderate temperatures. In the latter case, hydrogen sulfide is evolved, and this gas accompanies the Gulf Coast petroleums sometimes in very large quantities.

The Formation of the Paraffines.

Decomposition of a wide variety of organic substances by heat yields paraffine hydrocarbons among the products so formed. Methane is an important constituent of retort coal gas (30 to 40%), by-product coke oven gas, oil gas and the like. The per cent of methane contained in such gases depends upon many factors, for example temperature, the duration of the heating and the presence or absence of substances capable of affecting the equilibria in such gas systems.[83] Thus in the coking of coal the gas is richest in methane when the retort temperature is within the range 600° to 800° but as the retort temperature increases above 800° the per cent of methane in the evolved gas rapidly diminishes and the per cent of hydrogen rapidly increases.[84] Gases containing ethylene, such as oil gas and coal gas, are invariably not in equilibrium at the temperatures at which they are produced and in practice they are removed and cooled before equilibrium at the higher temperature is established. Ethylene is rapidly decomposed, above 600° to methane and carbon and this reaction may be greatly catalysed by contact with iron oxide or other catalysts. Fats or fatty acids readily break down on heating under pressure to a series of hydrocarbons, mainly saturated, which closely resemble crude petroleum and Engler,[85] has used this fact in developing his theory of the origin of petroleums. It has been shown that in the heat decomposition of heavy, high boiling mineral oils under pressure, the lighter oils so produced

[83] Slator, *J. Chem. Soc.* *109*, 160 (1916).
[84] Vignon, *J. Gas Lighting* *121*, 107; Meyer, *Chem. Abs.* 8, 2795 (1914).
[85] *Petroleum* 7, 399 (1912).

consist largely of hydrocarbons of the paraffine series, which may be accounted for by the supposition that when a large paraffine molecule breaks up into two simpler molecules, one will be a saturated paraffine and the other an olefine,

$$\mathrm{R\ CH_2CH_2} \vdots \mathrm{CH_2\ R} \longrightarrow \mathrm{R\ CH_3 + CH_2{=}CH.R}$$ [86]

The destructive distillation of bituminous shales, lignites and peat yields distillates containing paraffine hydrocarbons; and paraffine wax has for many years been manufactured from the distillates of shale in Scotland. By the distillation of ordinary bituminous coking coal at low temperatures a distillate rich in paraffine wax is obtained. These solid paraffines like those from petroleum are normal hydrocarbons of 24 to 29 carbon atoms.[87]

Effects of Heat on Non-Benzenoid Hydrocarbons.

The changes brought about by heating non-benzenoid hydrocarbons have long been of industrial interest and importance, particularly in the manufacture of oil gas, carburetted water gas, the pyrolysis of petroleum oils for the manufacture of kerosene and more recently gasolene or motor fuel from heavier hydrocarbons. These processes are problems of technology or engineering, rather than chemistry, but more recently a desire to know more concerning the chemical reactions involved and their relationships has been indicated by the character of many of the published researches.

The two fundamental reactions which take place when hydrocarbons are heated to the decomposition point are, first, the rupture of the carbon-to-carbon structure and second, the dissociation of hydrogen from carbon. These two reactions probably occur simultaneously attended by a sequence of other reactions, but special catalysts may greatly accelerate one or the other type of reaction, for example, nickel, palladium or platinum may cause dissociation of hydrogen without alteration of the carbon structure, as in the conversion of cyclohexane to benzene in the presence of nickel at 250°, or the complete rearrangement and splitting of hydrocarbons by gentle heating in the presence of anhydrous aluminum chloride, in which case methane but not hydrogen is evolved.

The earlier technical investigations of the pyrolysis of hydrocar-

[86] Olefines of this type are unstable and rearrange. cf. pp. (150, 151).
[87] Glund, *Ber.* 52, 1039 (1919).

bons centered upon coal tar, benzene, naphthalene and their derivatives. In 1866-7, Berthelot published a series of important researches,[88] and stated that at a "dull red heat" equilibrium was established between ethylene, hydrogen and ethane. He discovered a series of condensations of acetylene; that in the presence of coke, acetylene, at the "temperature at which glass softens" is decomposed almost wholly to hydrogen and carbon; acetylene and ethylene yield a condensation product isomeric, or identical with crotonylene, and acetylene and benzene gave naphthalene. Benzene passed through a porcelain tube gave diphenyl, chrysene and a resinous substance, but no anthracene or naphthalene. Toluene gave benzene, unchanged toluene, and large proportions of naphthalene. Xylene gave toluene as the principal product. Berthelot's view that acetylene was the parent substance of the benzenoid hydrocarbons was vigorously disputed by Thorpe and Young,[89] Armstrong and Miller [90] and Haber [91] who considered that hydrogen or methane were first formed, the residues then condensing or undergoing still further decomposition:

$$2\ C_6H_6 \longrightarrow C_{12}H_{10}(\text{diphenyl}) + H_2$$
$$C_6H_{14}\ (\text{hexane}) \longrightarrow C_5H_{10}(\text{amylene}) + CH_4$$

They pointed out that usually acetylene cannot be detected among the products of pyrolysis. Bone and Coward [92] have made a careful study of the thermal decomposition of methane, ethane, ethylene and acetylene and concluded that Berthelot's theory of the attainment of equilibrium between dissociation and recombination of these hydrocarbons is not borne out by the experimental evidence. Their results show:

(1) Methane is exceedingly stable. It decomposes almost exclusively into hydrogen and carbon and this decomposition, though reversible, is mainly a *surface* phenomenon, at least at moderate temperatures.

(2) Acetylene polymerizes at comparatively low temperatures, the optimum temperature range for this polymerization being 600°–700°. Acetylene being formed from ethylene, condensation products of acetylene will be found among the products whenever ethylene is a primary product of the pyrolysis of hydrocarbons.

[88] *Compt. rend.* ***62***, 905, 947 (1866); ***63***, 788, 834 (1866); *Bull. Soc. Chim.* (2) 7, 217 (1867).
[89] *Proc. Roy. Soc.* ***19***, 370; ***20***, 488; ***21***, 184 (1873).
[90] *Chem. News* ***49***, 285; *Soc.* ***49***, 74 (1886).
[91] J. Gasbel, ***39***, 377, 395, 435, 452, 799; *Ber.* ***29***, 2691 (1896).
[92] *Soc.* ***93***, 1197 (1908).

(3) Ethylene and acetylene combine with hydrogen at moderate temperatures to form ethane. Whitaker and Leslie [93] obtained evidence of hydrogenation at 620° when hydrogen was introduced with oil in an experimental apparatus for making oil gas. These authors also call attention to the fact that in decomposing oil to gaseous products, equilibrium, or rather the ultimate composition which a given temperature tends to produce, is seldom attained, even in apparatus of industrial size, owing to the short period of *time,* during which the hydrocarbons are subjected to the particular temperature of the operation. One reason for this undoubtedly lies in the fact that some of the reactions taking place in such systems are strongly endothermic, for example,

$$C_2H_6 \longrightarrow C_2H_4 + H_2 = 31{,}270 \text{ calories}$$

and such reactions can be maintained only by the absorption of a large supply of energy.[94]

It is well known that the velocities of chemical changes are greatly affected by relatively small changes in temperature. It is, therefore, readily understood that small differences of operating temperature may cause very great differences in the character of the pyrolytic products, a fact apparently first appreciated in industrial operations by Hall.

Generally speaking, the temperatures employed for obtaining motor fuel are within the range 410°–500° and Rittman, Dutton & Dean [95] consider that the maximum yield of aromatic hydrocarbons (from petroleum oils) is obtained within the range 650°–700°. Ipatiev [96] states that at 600°–700° hexane and cyclohexane yield olefines and other hydrocarbons, but no benzenoid hydrocarbons. Methyl cyclopentane was found among the products. Norton and Andrews [97] found that at 550° hexane was not decomposed and was very slightly affected at 600° but at 700° decomposition with formation of gas, methane and ethylene, propylene, butylene, amylene, hexylene and butadiene but no benzene. Iso-hexane and n.pentane show approximately the same stability and at 700° yield gas and a series of olefines. Benzene appears among the products of reaction only at higher temperatures. Thus Haber obtained benzene from hexane by heating to 800° [98] and Worstall and Burwell obtained it from heptane and octane at 900°.[99]

[93] *J. Ind. & Eng. Chem. 8,* 593, 684 (1916).
[94] Lomax, Dunstan & Thole, *J. Inst. Petr. Techn. 3,* 76 (1916).
[95] U. S. Bur. Mines Bull. 114, Washington (1916).
[96] *Ber. 44,* 1984, 2978 (1911).
[97] *Am. Chem. J. 8,* 1 (1886).
[98] Loc. cit.
[99] *Am. Chem. J. 19,* 815 (1897).

Benzene and its simple homologues had been found in the liquid condensate obtained by compressing oil gas.[100] Armstrong and Miller made a careful study of this liquid condensate from oil gas and identified propylene, amylene, hexylene, heptylene, crotonylene, isoallylethylene, benzene, toluene, xylenes, mesitylene, pseudo-cumene and naphthalene. In 1878, a number of processes were described [101] which sought to manufacture benzene hydrocarbons from Russian petroleum by passing the oil through red-hot tubes packed with various materials (the function of which was not evident). None of these processes were industrially successful. Nikiforoffs' process was apparently a development from the well known Pintsch gas process, the oil being first decomposed or vaporized at 525°–550° and then passed through retorts, similar to the older type of Pintsch gas retort, at 700°–1200° under a pressure of about two atmospheres. No further important work on the manufacture of benzene hydrocarbons from petroleum oils by the action of heat, in the absence of catalysts, was made until the recent war period when Hall, working in England, and Rittman and his coworkers in the United States, developed processes, which were operated industrially. Hall decomposes oil at 550°–600° and under a pressure of about 70 pounds per square inch when motor fuel is the desired product and for benzene and toluene the operating temperature is 750° and the pressures 100 to 110 pounds per square inch.[102] A noteworthy mechanical feature of the Hall process is very rapid passage of the oil and vapors through the heated tubes, which minimizes the deposition of carbon. Rittman employed a temperature of 700° and a pressure of 150 pounds per square inch. In connection with this work, which probably should be regarded as a war time industry, at least so far as the manufacture of benzene and toluene from petroleum is concerned, much valuable experimental work was done. Commercial gas oil, specific gravity 0.817 at 15.5° and boiling at 200°–350°, in the Rittman apparatus gave a maximum yield of toluene, 3.1 per cent by volume, at 650°. The maximum yield of benzene, 4.4 per cent by volume was obtained at 800°. The maximum yield of xylene was 1.9 per cent at 750°.[103]

Other conditions being equal, higher yields of aromatic hydrocarbons are obtained from petroleum containing relatively large pro-

[100] Armstrong and Miller, *J. Chem. Soc.* *49*, 74 (1886); Williams, *Chem. News* *49*, 197 (1884).

[101] Letny, *Ber. 11*, 1210 (1878); Liebermann & Burg, *Ber. 11*, 723 (1878); Salzmann & Wichelhaus, *Ber. 11*, 1431 (1878).

[102] U. S. Pat. 1,175,909; Brit. Pat. 24,491 (1913); 437 (1914); 2948 (1914); 7282 (1914); 12,962 (1914); 1594 (1915); U. S. Pat. 1,194,289; 1,175,910.

[103] Egloff, *Met. & Chem. Eng. 16*, 492 (1917).

portions of benzene and naphthalene derivatives and cyclohexane derivatives, such as Borneo petroleum. The oil from the deeper strata of the Kotei field in Borneo was used in England during the war for the manufacture of benzene and toluene. Jones and Wooton first called attention to the unusual character of this oil and more recently Chavanne and Simon [104] have examined the gasoline fraction of this oil and state that they have identified cyclopentane, methylcyclopentane, cyclohexane, a dimethylcyclopentane, methylcyclohexane and dimethylcyclohexane. During the war gasoline from this petroleum was sent to England where benzene and toluene were made from it in a fair degree of purity. This gasoline contained about 40 per cent of aromatic hydrocarbons of which about 7 per cent was benzene, 14 per cent toluene, 15 per cent xylenes and 4 per cent higher homologues.[105] Brooks and Humphrey [106] found small quantities of benzene and toluene in gasoline made by distilling heavy Oklahoma oil at the relatively low temperature of 420° and a pressure of 100 pounds per square inch. Small yields of aromatic hydrocarbons were also obtained from heavy high-boiling petroleums by heating with anhydrous aluminum chloride and since the temperature employed in the first method is considerably below that at which benzene has been observed to be formed from paraffines or naphthenes, they conclude that high boiling benzene derivatives are present in the original oil, benzene being obtained by their splitting or "cracking."

It was apparent from much of the early work on pyrolysis that the character of the products obtained was not solely a function of the temperature employed but also of the time or duration of the heating and also the presence or absence of various substances acting catalytically upon the decomposition, either hydrogen dissociation or splitting of the carbon structure, or affecting one or more of the secondary reactions, for example polymerization of the olefines which are formed. Before discussing the effect of catlysts the results of pyrolysis at moderate temperatures will be noted.

One of the most conspicuous differences in the results of low temperature decomposition is the greatly decreased yield of gas. Exact comparisons are difficult to make on account of variable time factors, different distribution and character of the heated surfaces and the like. Hall states that in the industrial tube type of apparatus developed by him a change of operating temperature from 540° to 580° results in an

[104] *Compt. rend. 1919,* 285.
[105] Kewley, *Chem. Tr. J. 1921,* 380.
[106] *J. Am. Chem. Soc. 38,* 393 (1916).

increase of 50 per cent in the quantity of gas obtained. In a small experimental pressure still Brooks, Padgett and Humphrey[107] found, when distilling 85 per cent of the oil used [heavy Oklahoma gas oil], under pressure, that at 50 pounds pressure and a mean temperature of 410°, 24.8 liters of gas were formed per liter of distillate; at 150 pounds pressure and a mean temperature of 425°, 58 liters of gas per liter of distillate were produced. The relative area of heated surface (iron) in this small apparatus was quite large, as compared with oil distilling apparatus of industrial dimensions of the Burton type, but the results are indicative of the large difference in gas yield resulting from a comparatively slight temperature change. The effect of increased pressure should, per se, decrease the gas yield by polymerizing the olefines. That higher temperatures give large proportions of olefines in the gas is indicated by the following table:

COMPOSITION OF OIL GAS MADE IN TUBES MAINTAINED AT DEFINITE TEMPERATURES.[108]

Temperature, deg. C	600.	650.	700.	730.
Pressure, lb.	57.	72.	83.	95.
Ethylene, per cent	19.3	19.0	17.7	17.5
Propylene, per cent	28.0	28.4	23.9	20.0
Higher olefines, per cent	3.2	4.2	3.5	3.1
Total olefines, per cent	50.5	51.6	45.1	40.6

GASES FROM CRACKING DISTILLATIONS UNDER 100-LB. PRESSURE.

From Jennings Crude

	1	2	3
	340°	415°	422°
Temperature in still	Per Cent	Per Cent	Per Cent
CO_2	1.2	0.5	0.0
CO	1.2	0.5	1.3
Illuminants	15.4	15.3	13.0
Hydrogen	0.0	4.0	4.4
Saturated Hydrocarbons	81.5	79.7	81.3

From Paraffine

	417°	432°	437°
Temperature in still	Per Cent	Per Cent	Per Cent
CO_2	0.0	0.0	0.0
CO	0.0	0.0	0.0
Illuminants	25.4	37.0	33.5
Hydrogen	0.3	0.9	3.0
Saturated Hydrocarbons	74.3	62.1	63.5

Analyses of oil gas are usually reported in terms of total olefines, or illuminants, hydrogen and methane. Accurate analyses, with respect to methane, ethane, propane and other hydrocarbons, made by the method of fractional distillation at low temperatures have not been re-

[107] *J. Frankl. Inst. 180,* 653 (1915).
[108] Hall type of apparatus, industrial size.

ported. The relative proportions of ethylene, propylene and other olefines in oil gas made at different temperatures in a commercial size Pintsch gas apparatus is given in the following table:

Per Cent Ethylene and Propylene in Oil Gas.

Temp. Deg. C	Higher Olefines Per Cent	C_3H_6 Per Cent	C_2H_4 Per Cent	Total Olefines Per Cent
805–650	1.4	18.6	16.3	36.3
660–535	1.6	19.0	18.3	38.9
635–535	2.4	22.4	12.5	37.3
625–535	2.6	22.6	13.7	38.5
615–425	3.8	25.7	12.0	41.5

The composition with respect to olefines of gas made at definite temperatures in a large industrial size apparatus of the Hall type is as follows: [109]

Per Cent Oil Gasified in Hall Type Apparatus at Different Temperatures.

Temperature Deg. C	Per Cent Gas	Per Cent Ethylene and Propylene
605	17.7	47.9
625	26.6	46.1
645	37.6	44.9
665	40.0	43.7
685	40.8(?)	42.6
705	48.7	39.5
725	66.6	38.5

Typical analyses of commercial gases are of interest particularly as regards the relative proportions of methane, ethane, hydrogen and illuminants.[110]

Average Composition of Commercial Gases.

	Illum. %	CO %	H_2 %	CH_4 %	C_2H_6 %	CO_2 %	O_2 %	N_2 %	Cdl. Pr.	B.T.U.
Coal gas	4.0	8.5	49.8	29.5	3.2	1.6	.4	3.2	16.1	622
Carburetted water gas	13.3	30.4	37.7	10.0	3.2	3.0	.4	2.1	22.1	643
Pintsch gas	30.0	.1	13.2	45.0	9.0	.2	.0	1.6	43.0	1276
Blau gas	51.9	.1	2.7	44.1	.0	.0	.0	1.2	48.2	1704
All oil water gas	7.0	9.2	39.8	34.6	..	2.6	.2	6.6	19.7	680
Oil gas	31.3	2.4	13.5	46.5	3.0	.3	.0	1.1	38.0	1320
Blue water gas	.0	40.9	50.8	.2	.0	3.4	.9	3.5	...	299
Producer gas (coal)	.2	17.6	10.4	6.3	.0	7.3	.7	58.1	...	161
Producer gas (coke)	.0	25.3	13.2	.4	.0	5.4	.6	55.2	...	137
Blast furnace gas	.0	26.5	3.5	.2	..	12.8	.1	56.9	...	100
Wood gas (pine)	10.6	27.1	32.7	21.5	..	4.9	.4	2.6	...	607
Oil gas, Dayton process[111]	14.7	5.6	1.7	7.8		6.1	..	63.2	...	500 / 300

[109] Brooks, *Chem. & Met. Eng. 22,* April 7, 1920.
[110] Rogers' *Industrial Chemistry* Ed. 2. Fulweiler, p. 474.
[111] Binnall, *Gas Age 47,* 47 (1921). This process depends upon the partial combustion of the oil sufficient to raise sufficient heat to gasify the remainder. About 4 gallons of oil are required to make 1000 cubic feet of gas of 450 B. T. U. The per cent of nitrogen is naturally high.

Although data obtained in making oil gas on a small experimental scale have no close industrial parallel, the experimental results of Whitaker and Rittman [112] are of interest as indicating the very marked effect of variations of temperature and pressure.

OIL GAS EXPERIMENTS OF WHITAKER & RITTMAN.*

Temp. °C	Pressure lb. per sq. in.	Gas Liters	Carbon Grams	Tar c.c.	CH_4 Liters	C_2H_6 Liters	H_2 Liters	Illum. Liters
650°	15.	135	3	163	45.5	13.8	12.1	58.8
650°	45.	145	8	133	65.2	16.7	13.1	44.3
750°	0.75	146	1	153	....	....	18.3	82.0
750°	15.	206	18	80	84.5	10.15	39.6	63.0
750°	45.	194	26	87	110.0	11.8	33.9	30.1
900°	0.75	235	12	58	63.4	trace	48.8	110.0
900°	15.0	382	115	11	178.1	trace	148.2	50.0
900°	45.0	310	165	9	128.9	none	155.0	15.5

*40cc Oil used.

In a later paper Whitaker and Alexander [113] showed that under the same experimental conditions the composition of the gas produced varies with the rate of oil feed, within rather wide limits, and that even at comparatively slow rates of oil feed equilibrium is not reached. Thus it has been shown that at 1200° hydrogen is in equilibrium with carbon and about 0.3 per cent methane, but Whitaker and Alexander find 6 to 10 per cent methane in their most slowly conducted experiments [114] and they emphasize the fact that equilibrium compositions are not obtained in gas making practice and that it would be impractical to run an oil gas generator at such rates of oil feed as would even approximate equilibrium conditions.

Zanetti [115] obtained typical oil gas by decomposing the *propane* fraction of natural gas gasoline at 750°, obtaining ethylene, propylene, butylene and small quantities of liquid hydrocarbons and tars.

In view of the fact that the coking of coal at low temperatures yields a distillate containing paraffine wax, naphthenes and olefines and resembling crude shale oil in its general character the coking of coal at higher temperatures with the formation of coal gas and typical coal tars should be regarded as essentially paralleling the high temperature pyrolysis of mineral oils, in contact with coke or carbon.

[112] *J. Ind. & Eng. Chem.* 6, 479 (1914).
[113] *J. Ind. & Eng. Chem.* 7, 484 (1915).
[114] The commercial manufacture of hydrogen by heating methane or other hydrocarbons to 1200°-1300° has been proposed, with various modifications, for example see Uhlinger, U. S. Pat. 1,363,488.
[115] *J. Ind. & Eng. Chem.* 8, 674 (1916).

As regards the liquid products of pyrolysis of high boiling hydrocarbons at moderate temperatures, low temperature, pressure and slow operation favor the formation of saturated low boiling hydrocarbons. Hall and others have called attention to the relatively large yields of olefines and diolefines obtained at 550°–600°. Such distillates are said to be "highly cracked," absorb oxygen readily, a very general property of diolefines (see pages 212, 216) forming a resinous oxidation product which is often noticed as a sticky film when such oil is permitted to evaporate. Such distillates, containing diolefines, react energetically with sulphuric acid forming tars. Slow distillation under pressure evidently *polymerizes* the olefines since hydrogenation of hydrocarbons at 400°–450° in the absence of catalysts and under moderate pressures has not been observed. Although Bergius has hydrogenated fatty oils in the absence of finely divided metallic catalysts by heating with hydrogen under 30 atmospheres,[116] no hydrogenation of unsaturated petroleum hydrocarbons could be detected by Brooks [117] on heating at 196° for 30 hours under a hydrogen pressure of 3000 pounds per square inch. However, Ipatiev [118] noted evidence of hydrogenation at higher temperatures and under pressures up to 340 atmospheres.

The low boiling hydrocarbons produced at moderate temperatures are mainly normal saturated paraffines as has been shown by Humphrey in the case of a distillate made from the heavy residues of Oklahoma petroleum by distilling at 400°–420° and 100 pounds pressure.[119] The presence of small quantities of benzene and its homologues in such distillates has been noted.

Among the diolefines, which have been identified in the low boiling fractions butadiene and isoprene have been repeatedly noted. The yield or relative proportions of these hydrocarbons obtainable in this way is quite small. Engler and Staudinger,[120] however, have patented the manufacture of these conjugated diolefines by the thermal decomposition of mineral oils. Pyrolysis under reduced pressure increases the proportion of unsaturated hydrocarbons, at least among the gaseous products.[121]

The polymerization of olefines by heating under pressure has been frequently observed. Ethylene, the most stable known olefine, is polymerized in the presence of iron at 380°–400° and 70 atmospheres

[116] *Z. angew. Chem. 1914,* 522.
[117] *J. Frank. Inst. 1915,* 658.
[118] *Ber. 37,* 2961 (1904).
[119] *J. Ind. & Eng. Chem.* 7, 180 (1915).
[120] German Pat. 265,172 (1912).
[121] Whitaker & Rittman loc. cit.

pressure, a complex mixture of hydrocarbons being formed.[122] The polymerization of conjugated diolefines at moderate temperature and pressures has been applied to the synthesis of rubber (see page 000) and Semmler[123] has condensed isoprene with limonene and other terpenes at 275° to form new sesquiterpenes of the empirical formula $C_{15}H_{24}$. Lebedev[124] has polymerized allene by heating in glass at 140° obtaining 5% dimeride, 15% trimeride and 80% of more highly polymerized material. Diallyl is very slowly polymerized at 250° to a dimeride and a gummy residue. At 150° 2 : 4 hexadine yields chiefly the dimeride. The polymerization of olefines is markedly catalyzed by many substances. Gurwitsch[125] polymerized amylene by fuller's earth at ordinary temperature and Hall polymerized the resin-forming constituents (diolefines) contained in light pyrolytic gasoline distillate, by passing the hot vapors through a column of fuller's earth. Fuller's earth, kaolin and alumina are said to slightly increase the yield of low-boiling hydrocarbons.

The effect of nickel in a finely divided condition in bringing about equilibrium conditions between unsaturated hydrocarbons, hydrogen and saturated hydrocarbons, has led to quite changed conceptions regarding the stability of hydrocarbons. The earlier work had to do almost exclusively with the formation of saturated hydrocarbons, with yields which were practically quantitative. The reversible nature of the reaction was not clearly recognized until Sabatier and Senderens showed that cyclohexane was converted into benzene in the presence of finely divided nickel at 270°–280°. Zelinsky[126] showed that cyclohexane and methylcyclohexane are reduced to benzene and toluene respectively, together with free hydrogen, by heating in the presence of finely divided palladium. The reaction is appreciable at about 190°, and within the range 200°–300°, the equilibrium mixture contains very large proportions of benzene.[127] No dihydro or tetrahydro derivatives were found among the reaction products. Hexane, cyclopentane and methylcyclopentane are more stable, and do not yield free hydrogen appreciably below 300°. The extraordinary stability of methylcyclopentane as compared with cyclohexane is shown by later experiments of Zelinsky, in which a mixture of methylcyclopentane and cyclohexane

[122] Ipatiev, *J. Russ.* *38*, I, 63 (1906).
[123] *Ber.* *47*, 2068, 2252 (1914).
[124] J. S. C. I. *1914*, 1224.
[125] *J. Russ.* *47*, 827 (1915).
[126] *J. Russ. Phys.-Chem. Soc.* *43*, 1220 (1911); *Ber.* *44*, 3121 (1911).
[127] Tausz & Putnoky, *Ber.* *52*, 1573 (1919), state that in the presence of palladium black the formation of benzene from cyclohexane is practically quantitative at 270°-300°. They confirm the absence of cyclohexane in Pennsylvania gasoline by testing for the formation of benzene under these conditions.

were passed over palladium black at 300°, until no further hydrogen was evolved. The cyclohexane was converted to benzene, thus offering a convenient and easy method of separating these two hydrocarbons.[128]

That these results are brought about by the catalysts is indicated by many observations, for example, Ipatiev [129] had shown previously, that benzene is not formed from cyclohexane or hexane on passing the vapors through an iron tube heated to 650°–700° C. At considerably lower temperatures, cyclohexane is readily formed from benzene, the reaction being very rapid in the presence of finely divided nickel and hydrogen at 160°. The catalytic effect of iron, copper and aluminum on the dissociation or addition of hydrogen is very slight. Whether or not the iron surface of pressure stills and similar apparatus have any catalytic effect on the pyrolytic changes effected by heating petroleum oils is not certain, but since very finely divided iron has only a very slight effect, the catalytic effect of the iron or steel surfaces of industrial apparatus is probably negligible.

It has frequently been proposed to insert catalysts into pressure stills and similar apparatus with the object of hydrogenating the olefines which distillates made in this way normally contain, but these methods have had no technical success. Nickel, the most active catalyst of this type, is very quickly covered with coke and thereby rendered inactive.[130] Sabatier and Mailhe proposed to remove the carbon from the metal catalyst by heating in a current of steam.[131]

The lower temperatures at which the reaction of steam and carbon becomes appreciable have not been determined and this doubtless varies considerably with different forms of carbon. Bergius has converted carbon and water to hydrogen and CO_2 by heating at 300° and 150 atmospheres pressure for 20 days. Although water gas has been manufactured for many years, high temperatures are always employed since it has long been known that low temperatures favor the formation of CO_2 in the gas equilibrium $CO + H_2O \leftrightarrows CO_2 + H_2$.[132] A number of patents have described the decomposition of heavy oils in the presence of steam and one patentee claims that iron acts as a catalyst in this steam-hydrocarbon mixture.[133] This process has been carried out on a

[128] *Ber.* *45*, 678 (1912).
[129] *Ber.* *44*, 2987 (1911).
[130] The manufacture of hydrogen from methane in the presence of nickel at 700° as proposed in the Badische process, French Pat. 463,114 (1913), is undoubtedly subject to this difficulty.
[131] U. S. Pat. 1,152,765 (1915); U. S. Pat. 1,124,333 (1915).
[132] Taylor & Rideal: Catalysis, p. 158.
[133] Noad & Townsend, Brit. Pat. 113,675 (1908).

fairly large scale, the tubes or retorts being packed with iron turnings and a temperature of about 600° maintained. Greenstreet claims that the presence of steam in the zone of decomposition prevents the deposition of carbon or reacts with the carbon to form carbon monoxide and hydrogen, the hydrogen being supposed to be taken up by the unsaturated hydrocarbons. In the presence of nickel, Sabatier observed the reaction of steam and carbon to CO_2 and hydrogen at 500°.

The only catalytic process which has shown great industrial promise is of an altogether different type from the catalysts discussed in the foregoing paragraphs. Abel and also Friedel and Crafts described the decomposition of petroleum hydrocarbons by heating with anhydrous aluminum chloride.[134] Gustavson noted a similar behavior with aluminum bromide. Heusler noted that unsaturated hydrocarbons are polymerized by aluminum chloride and also that sulfur derivatives are decomposed and the sulfur removed.[135] Aschan also noted the polymerization of olefines in the presence of this reagent and Engler observed that amylene, heated with anhydrous aluminum chloride,[136] yielded a mixture of polymers resembling natural lubricating oil.

A number of patents have been recently issued to McAfee,[137] who has determined the technical refinements necessary in the utilization of this catalyst. In addition to a little gas and a mixture of volatile saturated hydrocarbons including an excellent grade of gasoline, a heavy viscous residue is formed, which contains the greater part of the aluminum chloride. This material is very readily carbonized when heated, and the recovery of aluminum chloride from these residues is the really difficult part of the problem, at least from a technical and economical standpoint. The effect of anhydrous zinc chloride and anhydrous ferric chloride is similar but much less effective.

Synthesis of the Paraffines.

The reduction of alkyl halides (chlorides, bromides or iodides) by nascent hydrogen has been accomplished in a number of ways. The method of Gladstone and Tribe [138] of reducing alkyl iodides in alcohol solution by the copper-zinc couple has been most fruitful. Many of these earlier methods were discovered in the attempt to isolate the so-called radicals; for example, Frankland showed that heating the simpler alkyl iodides with water and zinc gave the corresponding hydro-

[134] Friedel & Crafts, *Compt. rend. 100,* 692; Gustavson, *J. prakt. chem. 34,* 161; Egloff & Moore, *Met. & Chem. Eng. 15,* 67, 340 (1916).

[135] Brit. Pat. 4769 (1877).

[136] *Z. angew. Chem. 9,* 288, 318 (1896); *Ber. 42,* 4613 (1909).

[137] U. S. Patent 1,099,096; 1,127,465 and 1,144,304.

[138] *Ber. 6,* 202, 454, 1136, 1873; *J. Chem. Soc. 45,* 154 (1884).

carbons, possibly through the intermediate formation of zinc dialkyls. When pure zinc dialkyls are treated with water very energetic decomposition occurs with the formation of a hydrocarbon and zinc hydroxide.

$$Zn(C_2H_5)_2 + 2H_2O \longrightarrow Zn(OH)_2 + 2C_2H_6$$

This method has been displaced by the well-known Grignard reaction, the simpler alkyl halides readily yielding alkyl magnesium halides which are quantitatively decomposed by water to give hydrocarbons.

$$C_2H_5Br + Mg + (C_2H_5)_2O \longrightarrow C_2H_5MgBr.(C_2H_5)_2O$$

$$C_2H_5MgBr.(C_2H_5)_2O + H_2O \rightarrow Mg\begin{matrix} \diagup OH \\ \diagdown Br \end{matrix} + C_2H_6 + (C_2H_5)_2O$$

Ammonia or an amine may be employed instead of water to decompose the magnesium complex. It should be pointed out, however, that another reaction takes place with magnesium and alkyl halides which, though a very subordinate reaction in the case of the simpler alkyls, becomes the principal result with halogen derivatives containing six or more carbon atoms.[139] Thus, like the condensation of propyl bromide by metallic sodium to form n.hexane, propyl bromide and magnesium, in ether, yields a small amount of n.hexane as expressed by the reaction,

$$C_3H_7Br + Mg \longrightarrow C_3H_7MgBr$$
$$C_3H_7MgBr + C_3H_7Br \longrightarrow MgBr_2 + C_6H_{14}$$

This reaction is an admirable method of synthesis within certain limits.[140] Thus in the terpene series halides such as bornyl chloride react so slowly with magnesium that the Grignard reactions are of practically no value for halogen derivatives of this class. Hydrocarbons of an odd number of carbon atoms may be synthesized by a slight modification of the method, for example,

$$C_3H_7MgBr + C_4H_9Br \longrightarrow MgBr_2 + C_7H_{16}$$
$$C_4H_9MgBr + C_5H_{11}Br \longrightarrow MgBr_2 + C_9H_{20}$$

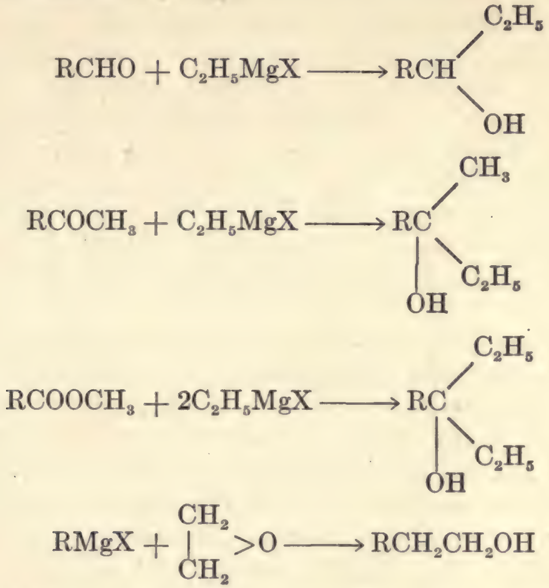
A modification of the above method has proven most satisfactory for the preparation of tetramethyl methane, the magnesium complex $(CH_3)_3C.MgI$ being treated with methyl sulfate.[141]

[139] Grignard & Tissier, *Compt. rend. 132,* 835 (1901).

[140] Alkyl groups may be introduced in the benzene ring by treating magnesium phenyl bromide with propyl or allyl bromide. Tiffeneau, *Compt. rend. 145,* 437 (1907); Kling, *Compt. rend. 137,* 756 (1903); Brit. Pat. 122, 630 (1919).

[141] Ferrario & Fogetti, *Gazz. Chim. Ital. 38,* II, 630 (1908).

The Grignard reaction has a wide range of usefulness in building up substances having the carbon atom structures of the hydrocarbons desired, the hydrocarbons themselves then being obtained by other methods, for example,



the alcohols thus obtained being converted to hydrocarbons by means of the corresponding iodide and reduction, or by decomposing the alcohols or corresponding halides to olefines and hydrogenating the latter.

Hydriodic acid has been widely employed for the purpose of energetic reduction. Berthelot[142] heated alcohols or alkyl halides with concentrated hydriodic acid in sealed tubes and discovered that reduction occurs as follows,

$$C_2H_5I + HI \longrightarrow C_2H_6 + I_2$$

Fatty acids may be reduced to paraffines of the same number of carbon atoms by this method and Krafft[143] prepared the normal paraffines from nonane to tetracosane, $C_{24}H_{50}$, by converting the ketones, made through the lime salts of the fatty acids, into the corresponding chlorides and reducing the latter with hydriodic acid (in the presence of red phosphorus).

$$(C_{10}H_{21})_2CO \longrightarrow (C_{10}H_{21})_2CCl_2 \longrightarrow (C_{10}H_{21})_2CH_2 \text{ or } C_{21}H_{44}$$

[142] *J. prakt. chem.* (1), *104*, 103 (1868).
[143] *Ber. 15*, 1687, 1711 (1882); *19*, 2218 (1886).

Magnesium amalgam has been employed for the reduction of alkyl halides by Meunier [144] and Wislicenus showed that the aluminum-mercury couple is of wide applicability.[145] Thus isobutyl, n.butyl and n.propyl iodides, treated with the aluminum-mercury couple, give the corresponding hydrocarbons in nearly quantitative yields in a few hours at ordinary temperatures, as compared with heating for 80 to 90 hours as is necessary with the copper zinc couple. Clemmensen has recently shown that ketones and aldehydes are readily reduced to hydrocarbons by the zinc-mercury couple and hydrochloric acid.[146] Zelinsky [147] has employed the zinc-palladium couple and alcoholic hydrochloric acid with particularly good results in the case of iodine derivatives of cyclohexane and cyclopentane. Ordinarily, alkyl iodides give fair yields of the paraffines by reducing with zinc dust in acetic acid.[148]

The classical researches of Sabatier and Senderens have shown that ethylene and its homologues may be converted into the corresponding hydrocarbons by hydrogen in the presence of nickel or nickel oxide. With ethylene, copper appears to give the best results.[149] Ipatiev also employed copper at 300° for the catalytic hydrogenation of trimethylethylene to pure isopentane.[150] Brochet and Cabaret [151] showed that alpha-octene is readily hydrogenated in the presence of active nickel and at atmospheric pressure, at temperatures as low as 65°. At 160° β-hexane and β-octene are rapidly hydrogenated but above 200° decomposition occurs with rupture of the carbon chain. The methene group $> C = CH_2$, as in substances containing the allyl group, are more readily hydrogenated than other ethylene types.[152] Limonene, in the presence of copper, is hydrogenated to dihydrolimonene, only the Δ 8.9 group becoming saturated. Platinum black is generally not as effective in catalyzing hydrogenation as nickel and copper, but, with this catalyst also, the methene group is more easily reduced than other types. For example at 260° propylene is quickly reduced to propane and alpha-octene is rapidly hydrogenated at 215° but trimethylethylene and beta-hexene are not affected under these conditions.[153] The relative ease with which the methene group and

[144] *Compt. rend. 134,* 473 (1902).
[145] *J. prakt. Chem.* (2), *54,* 18 (1896).
[146] *Chem. Zent. 1913,* II, 255.
[147] *Ber. 31,* 3205 (1898).
[148] Wislicenus, *Ann. 219,* 312 (1883).
[149] Sabatier and Senderens, *Compt. rend. 130,* 1559 (1900) ; *134,* 1127 (1902).
[150] *Ber. 42,* 2089 (1909) ; *43,* 3387 (1910).
[151] *Compt. rend. 159,* 326 (1914).
[152] Albright, *J. Am. Chem. Soc. 36,* 2188 (1914).
[153] Sabatier and Senderens; *Compt. rend. 124,* 1358 (1897) ; *130,* 1761 (1900) ; *131,* 40 (1900) ; *134,* 1127 (1902).

other olefine types are hydrogenated by the action of sodium and alcohol is just the reverse of the results noted above. Thus isoeugenol, isosafrol and isoapiol are very readily hydrogenated by sodium and alcohol but their isomers, containing the methene or allyl group, are not.[154]

Although the catalytic hydrogenation or "hardening" of fatty oils[155] has become of great industrial importance, unsaturated or "cracked" petroleum distillates have not been successfully treated in this manner, at least not industrially.[156] It is very difficult to remove all of the sulfur from petroleum distillates and very small traces of this element are sufficient to poison the ordinary nickel catalyst. Rubber, prior to vulcanization and free from sulfur, does not appear to have been hydrogenated; oily saturated hydrocarbons might result.

Unstable cyclic hydrocarbons or naphthenes might be hydrogenated with rupture of the ring, after the manner of the formation of isopentane from methylcyclobutane by hydrogen and nickel at 200°.[157]

By employing relatively high pressures, about 30 atmospheres, Bergius has hydrogenated fatty oils at 300° without a catalyst.[158] Whether or not unsaturated hydrocarbons derived from petroleum would also be hydrogenated under these conditions has not been determined but they are evidently not affected at 196° and 3000 pounds hydrogen pressure per square inch.[159] Whitaker and Rittman[160] in the production of oil gas at temperatures within the range 750° to 800° obtained distinct evidence of hydrogenation of the gaseous olefines when hydrogen was introduced into the mixture, particularly when operating at increased pressures.

The platinum metals, when in a colloidal state of subdivision, are particularly useful in hydrogenating olefines on a small scale or in the laboratory. Since the reaction is quantitative, they have been frequently employed to determine the number of olefine bonds in a substance. The development of this method is due chiefly to Paal, Skita and Willstätter. Colloidal palladium, prepared according to Paal and Skita,

[154] Ciamician and Silber; *Ber.* **23**, 1162, 2285 (1890); Klages, *Ber.* **32**, 1436 (1899).

[155] Cf. Ellis, "The Hydrogenation of Oils," *1919*; Erdmann, *J. prakt. Chem.* (2), *91*, 469 (1915); Paal, *Ber.* *41*, 2273 (1908); Skita, "Katalytische Reduktion," 1912; Sabatier, "La Catalyse," 1913.

[156] Cf. Ubbelhode, *Petroleum* 7, 9, 334 (1912); Brooks, Bacon, Padgett and Humphrey; *J. Ind. & Eng. Chem.* 7, 180 (1915).

[157] Zelinsky; *J. Soc. Chem. Ind.* **32**, 216 (1913); Philipow, *J. prakt. Chem.* (2), **93**, 162 (1916).

[158] *Z. f. angew. Chem.* *1914*, 522.

[159] Brooks, Bacon, Padgett and Humphrey; *J. Ind. & Eng. Chem.* 7, 180 (1915).

[160] *J. Ind. & Eng. Chem.* *6*, 479 (1914).

is sensitive to acids but Willstätter,[161] Halse[162] and others have used colloidal platinum in glacial acetic acid. Under certain conditions palladium may also be used in acetic acid.[163]

The distillation of fats under pressure has already been referred to. The alkali *salts of the simpler fatty acids* yield paraffines when heated with caustic alkali or soda-lime.

$CH_3CO_2Na + NaOH \longrightarrow Na_2CO_3 + CH_4$. This reaction does not take place to any extent with the higher fatty acids but fairly good yields of the paraffines are obtained by heating the alkali salts, or soaps, with sodium methylate *in vacuo*.[164]

Kolbe's electrolytic synthesis has often been cited but has been of very little preparative value. Thus, on electrolysing an aqueous solution of sodium acetate the chief products are ethane, CO_2 and hydrogen.[165] In general the electrolysis of a fatty acid salt yields, in addition to the saturated hydrocarbon, an ester and an olefine. For example, sodium propionate gives butane, ethylene, ethyl propionate, carbon dioxide and hydrogen. The higher fatty acids salts yield a mixture of reaction products of the same character.[166] Aldehydes have been converted into the corresponding hydrocarbons by electrolytic reduction but the yields are very poor.[167]

The well-known method of Würtz, consisting in heating alkyl bromides or iodides with sodium, has had wide application in laboratory syntheses and it should be particularly pointed out that the reaction proceeds easily and with good yields with alkyl halides of high molecular weight. Alkyl chlorides have seldom been employed for this synthesis although Nef and others have called attention to the fact that alkyl bromides and particularly *iodides* have a much greater tendency to decompose to olefines, as in the ether reaction.

$$C_4H_9I + C_2H_5ONa \begin{array}{l} \nearrow C_4H_8 + NaI + C_2H_5OH \quad \text{(main reaction)} \\ \searrow C_4H_9 . O . C_2H_5 + NaI \end{array}$$

The Würtz synthesis has also been useful in ring closing and in the synthesis of numerous derivatives of cyclic hydrocarbons of both the ben-

161 *Ber.* *45*, 1471 (1912).
162 *J. prakt. Chem.* (2) *92*, 40 (1915).
163 Kelber, *Ber.* *45*, 1946 (1912).
164 Mai: *Ber.* *22*, 2133 (1889).
165 Kolbe, *Ann.* *69*, 257 (1849).
166 Peterson, *Z. f. Elektrochemie*, *12*, 141 (1906).
167 Scheps, *Ber.* *46*, 2565 (1913).

zenoid and non-benzenoid type. Normal hexacontane, $C_{60}H_{122}$, the longest normal carbon chain compound known, was made by means of this reaction.[168] Optically active hydrocarbons have been prepared by employing the iodides of optically active alcohols.[169]

[168] Hell and Hägle, *Ber.* **22**, 502 (1889).

[169] It should be pointed out that the only satisfactory methods of preparing pure alkyl mono halides are those which utilize the corresponding alcohols. To obtain the primary halides, or alcohols, recourse is often had to the reduction of fatty acid esters by sodium and absolute alcohol, according to Bouveault and Blanc (German Pat. 164,294 (1903). The addition of halogen acid to alpha-olefines gives mainly secondary halides ($R.CHX.CH_3$.)

Chapter II. Chemical Properties of Saturated Hydrocarbons

(1). Oxidation.

The oxidation of saturated hydrocarbons by oxygen, or air, and other oxidizing agents is important in several respects, for example,—the oxidation of lubricating oil in air compressors, the oxidation and carbonization of lubricating oils in automobile or other types of internal combustion engines, the oxidation and resinification of transformer oils, the bleaching of oils by air and sunlight and finally the oxidation of paraffine and other hydrocarbon mixtures to fatty or soap forming acids. Unfortunately very little research has been carried out with pure specimens of different types of hydrocarbons with the result that we know very little regarding their relative ease of oxidation. However some of the work recorded, having had to do with commercial products, is of industrial, if not scientific interest.

As long ago as 1868 Bolley noted that paraffine wax absorbs oxygen at 150° but he made no particular study of the matter.[1] Others noted that when air is passed through hot mineral oils small quantities of acetic and other simple fatty acids are formed.[2] Holde noted the oxidation and thickening of mineral lubricating oils when heated in thin layers for 10 hours at 100° [3] and in 1896 Byerly and Mabery described their now well-known process of manufacturing "artificial asphalt" by blowing air through heavy high boiling petroleum residues for four to five days at about 230°. The reaction is strongly exothermic and the temperature may rise to 300°–400° at the end of the operation. Water is formed during the process and very little oxygen remains in the final product, typical specimens showing 1.90 to 2.20 per cent oxygen. The bromine absorption values of the product are also low, ordinarily amounting to 14.0 to 19.0. The hardness and other physical properties of this asphalt would seem to indicate that considerable polymerization or condensation takes place during the process. Intermediate products

[1] *Z. f. Chemie, 1868,* 500.
[2] Zaloziecki, *Z. angew. Chem. 1891,* 416; Engler & Bock, *Chem. Ztg. 16,* 592 (1892).
[3] *J. Soc. Chem. Ind. 13,* 668 (1894); *14,* 174 (1895).

containing oxygen are undoubtedly formed, which may condense with the elimination of the water which is always observed. At lower temperatures oxidation by air has a markedly different result: oxygen is absorbed forming fatty or naphthenic acids and some resinous matter. It would appear that at the higher temperatures employed by Byerly and Mabery the oxidation products first formed, conceivably alcohols, aldehydes and ketones, condense with the elimination of water, but at lower temperatures, these primary oxidation products are subjected to further oxidation to fatty or naphthenic acids.

According to Worrall and Southcombe [4] lubricating oil may be heated to 750° F. in the presence of steam without causing resinification or other chemical change (although it may be noted that this is approximately the temperature employed by Burton for cracking heavy oils to gasoline).

The resinous oxidation product which is slowly formed on heating mineral oils to 100°–150° in contact with air, may partially be precipitated by petroleum ether. The resin behaves as an acid and may be removed by shaking out with alcoholic alkali. Kissling [5] associates this resin with carbonization and for testing purposes has proposed the determination of "tar numbers" and "coke numbers" of lubricating oils, after heating to 150° for 50 hours under standardized conditions.[6]

Transformer oils deteriorate by air oxidation particularly when the oil becomes heated as is usually the case when in service. As is indicated above, *water,* carbon dioxide, acid resinous material and simple fatty acids are formed. The latter are sometimes found in much used transformer oils in the form of iron or copper soaps, small quantities of which remain dissolved in the oil, and also in the form of insoluble basic salts or "sludge." Digby [7] states that these metallic soaps probably act catalytically in promoting the oxidation. Waters states that "These substances (resinous) are oxidation products, and are most efficient oxygen carriers." . . . "By heat they become polymerized and changed into asphaltic matter." "If they are not removed (as by filtration through fuller's earth or bone black) heating the oil in the air produces more asphalt than would otherwise be the case." A particular specimen of a typical resinous deposit showed 76.0 per cent carbon and 7.1 per cent hydrogen. The practical importance of the matter is apparent from the fact that 0.06 per cent of water in a transformer oil

[4] *J. Soc. Chem. Ind. 24,* 315 (1905).
[5] *Chem. Ztg. 30,* 932 (1906); *31,* 328 (1907); *32,* 938 (1908); *33,* 521, (1909).
[6] Compare Waters, U. S. Bur. Standards Bull. 7, 365 (1911); Circular *99* (1920).
[7] *J. Inst. Elec. Eng. 53,* 146 (1915).

reduces its dielectric resistance to about 50 per cent of the value for the same oil when dry.[8] Pure paraffine oil can hold this amount of water in solution and commercial transformer oils are able to hold in solution three to four times this proportion of water. Waters [9] noted the formation of 0.89 per cent of water in a lubricating oil exposed to air and light for 22 days. Light, however, accelerates oxidation by air. The above observations were carried out with refined commercial oils, but small percentages of olefine hydrocarbons were undoubtedly present in all the specimens investigated, since refining as ordinarily carried out with concentrated sulfuric acid does not remove all the olefines, the polymers thereby formed remaining in the oil. Generally olefines are more rapidly oxidized by air than saturated hydrocarbons, but Waters found that, of several oils examined by him, the one having the largest per cent of unsaturated hydrocarbons, as indicated by the iodine number and Maumené test, showed the least oxidation. Waters suggests that these differences may have been due to greater amounts of catalysts or oxygen carriers in the oxidized oils. The conclusion which may be drawn, however, is that factors other than the presence of olefines are of primary importance. On account of its decomposing action on resins and similar oxidized material, and its energetic action on unsaturated hydrocarbons, it is possible that oils refined by anhydrous aluminum chloride would be more stable and more resistant to oxidation in service as transformer oils than those oils which have been refined in the usual way with sulfuric acid.

Although the accelerating effect of sunlight on oxidation by air is taken advantage of in the industrial sun bleaching of mineral oils, no study of individual hydrocarbons appears to have been made. Ciamician and Silber [10] succeeded in oxidizing the methyl groups of toluene and xylene to the corresponding acids by air under the influence of sunlight. In the case of non-benzenoid hydrocarbons the group $\genfrac{}{}{0pt}{}{R}{R}{>}CH_2$ and R_3CH, would probably be oxidized rather than methyl groups.

It has been shown by the well-known work of Engler and Weissberg [11] that organic substances, which alone are not appreciably affected by air or oxygen, may readily be oxidized in the presence of a

[8] The method advocated by C. E. Skinner, of purifying old transformer oils by quick-lime, removes both water and fatty acids.
[9] Loc. cit.
[10] *Ber.* 45, 38 (1912).
[11] Vorgänge der Autoxydation, Brunswick, 1904.

second substance which is capable of direct oxidation. They have shown that the latter class of substances form peroxides and their hypothesis is that these peroxides may then effect the oxidation of substances which by themselves are inert to oxygen. Thus paraffine wax is only very slowly affected by air or oxygen at 150° but the oxidation is very much accelerated if a small quantity of previously oxidized material is introduced. Unsaturated hydrocarbons which are capable of forming peroxides, according to Engler's theory

$$\mathrm{RCH = CHR_1 + O_2 \longrightarrow \underset{\diagdown\, O_2\, \diagup}{RCH \text{——} CHR_1}}$$

may in this way bring about the oxidation of saturated hydrocarbons. Based upon this theory the oxidation of paraffine has been brought about by first chlorinating at 160° followed by decomposition of these chlorides by heating to 300° and then oxidizing to fatty acids.[12] Organic peroxides are decomposed by moisture which explains the finding of Charitschkoff mentioned above. Thus linseed oil shows greater increase in weight on "drying" in dry air than in moist air, at least during the first few days' exposure.

The oxidation of paraffine wax by air at 120° and 150° was noted as long ago as 1868,[13] but under the stress of the conditions prevailing in Central Europe during the war intensive research on the synthesis of fatty acids was carried out by a special commission of the German government, presided over by C. Engler. Numerous researches of the same character were undertaken by private concerns and a number of patents and published papers have recently appeared dealing with this subject. The statements of different investigators regarding the effect of metallic oxides and other substances introduced as catalysts is very contradictory but the most complete results published up to the present time indicate that the best yields are obtained without the addition of any catalytic material other than a small amount of previously oxidized material added to initiate the reaction.[14] The use of air under pressure accelerates the oxidation[15] but the substitution of oxygen for air causes the reaction to proceed too rapidly and peroxides are formed and accumulate to such an extent that violent explosions are apt to occur. When the oxidation is slowly and carefully carried out waxy esters of the fatty acids and higher alcohols, formed

[12] Schaarschmidt & Thiele, *Ber.* *53B*. 2128 (1920).
[13] Bolly & Tuchschmidt, *Z. f. Chemie*. 1868, 500; Jazukowitsch, *Ber.* *8*, 768 (1875).
[14] Grün. Ulbrich & Wirth, *Ber.* *53B*. 987 (1920).
[15] Löffl, *Chem. Ztg.* *44*, 561 (1920). Schneider, *J. Soc. Chem. Ind.* *40*, 141A. (1921), uses tubular retorts and air under 70 atmospheres pressure.

evidently as intermediate products, may be isolated from the oxidized mixture.[16] The oxidation to fatty acids, with yields amounting to approximately 86 per cent of the theory, takes place in a remarkably short time, this yield being obtainable in 12 hours at 160° in the absence of catalysts. In a normal oxidation the peroxides noted above are decomposed, probably assisting in the oxidation in the manner indicated by Engler and Weissberg. Carbon dioxide, formic, acetic and other simple, volatile fatty acids are formed and the yield of these appears to vary within wide limits, one of the "tricks" of the process being so to conduct the oxidation that only small proportions of these malodorous acids are formed. Presumably these volatile acids are removed by blowing with live steam, the residue having an acid number of 180 to 200, being then neutralized by alkali and the unsaponifiable portion returned for further oxidation. According to Löffl [17] acids satisfactory for soap manufacture have not yet been obtained, the addition of 10 to 20 per cent of cocoanut or palm oil being necessary to produce a soap of the desired detergent qualities. According to Löffl 120° is the best working temperature with air under about 45 pounds pressure. The presence of water, continually introduced with the air in the form of steam, favors the production of the higher fatty acids and in the absence of water or its removal as fast as formed the product is highly colored and partially resinified. As is usual in such cases a large number of special patents have appeared [18] claiming special advantages for various catalysts and other minor details of operation although the general process seems to have been broadly covered by previous publications, particularly the patent of Schaal.[19] Most of the published work on this subject has had to do with the oxidation of paraffine wax, probably with the idea of manufacturing fatty acids identical with fatty acids occurring in natural fats and oils, but in view of the much larger quantities of liquid naphthenic hydrocarbons of fifteen to twenty carbon atoms (present in kerosene and the intermediate or fuel oil distillates) and the lower cost of such material, it would seem highly desirable to study the oxidation of such oils under similar conditions. Although the carboxylic acid derivatives of the naphthenes as exemplified by the Russian naphthenic acids, have objectionable and very persistent odors, it is probable that these cyclic

[16] Grün. Ulbrich & Wirth. *Ber.* *53B.* 987 (1920).
[17] Loc. cit.
[18] Pardubitzer Fabr. Akt. Ges. f. Mineralölindustrie, Brit. Pat. 131,301; 131,302; 131,303; Schmidt, Brit. Pat. 109,386 (1907); Cf. also Fischer & Scheider, *Ber. 53*, 923 (1920); Kelber, *Ber. 53*, 66 (1920); Bergman, *Z. f. angew. Chem. 31*, I, 69 (1918); Holde, *Chem. Ztg. 78*, 447 (1920); Plauson, *Brit. Pat.* 156,141 (1919).
[19] Schaal, German Pat. 32, 705.

hydrocarbons would be decomposed by oxidation to open chain acids. Montan wax is more resistant to air oxidation than paraffine wax.[20]

Harries has applied his well-known method of ozonization to highly unsaturated oils such as the oily distillates obtained by the low temperature carbonization of coal and lignite.

When saturated hydrocarbons are burned with insufficient air for complete combustion, a little formaldehyde is formed. From a hexane fraction and isopentane Stepski [21] obtained water, carbon dioxide, formaldehyde, ethylene and small quantities of propylene, butylene and amylenes. The yields of formaldehyde and ethylene by known methods are too small for the process to be of industrial value.

The action of chemical oxidizing agents on saturated hydrocarbons shows that certain structures are more easily oxidized than others. Zelinsky and Zelikow [22] have noted that hydrocarbons of the type

$$\begin{matrix} R \\ & >CHR \\ R \end{matrix}$$

for example $(C_2H_5)_2CH.CH_3$ are readily oxidized by one per cent potassium permanganate solution. As contrasted with this, methane and ethane are only very slowly oxidized by five per cent permanganate solutions.[23] The hydrocarbon 2.6-dimethyloctane is fairly stable to permanganate at 100° but in the presence of unsaturated hydrocarbons (menthene) the dimethyloctane is oxidized rather rapidly even at 50°.[24] β-Butylhexane is rapidly oxidized by alkaline permanganate solution at 80° to 90°, but the only oxidation products which can be detected are carbon dioxide and formic acid: by oxidizing it at 25° a very small amount of butyric acid can be recognized.[25] Hydrocarbons of the type $R_1R_2R_3CH$ are also very easily oxidized by concentrated nitric acid, Sp. Gr. 1.53 but normal hydrocarbons, at ordinary temperatures are only very slowly acted upon. Less concentrated acid, Sp. Gr. 1.42 [26] gives a mixture of nitro derivatives and oxidation products of the normal hydrocarbons, and the least oxidation and maximum yields of nitro derivatives are obtained by heating, preferably in sealed tubes, with dilute nitric acid of 1.075 specific gravity.[27] Paraffine wax is slowly oxidized by nitrogen peroxide [28] at temperatures within the

[20] Schneider, *J. Soc. Chem. Ind.* *40,* 140A. (1921).
[21] *Monatsh.* *23,* 773 (1902).
[22] *Ber.* *34,* 2865 (1901).
[23] V. Meyer & Saam, *Ber.* *30,* 1438 (1897).
[24] Kishner, *J. Russ.* *45,* 1788 (1913).
[25] Levene & Cretcher, *J. Biol. Chem.* *33,* 505 (1918).
[26] Worstall, *Am. Chem. J.* *20,* 209 (1898) ; *21,* 213 (1899).
[27] Konowalow, *J. Russ. Phys.-Chem. Soc.* *27,* 418 (1895) ; *Chem. Zentr.* *1900,* I, 975.
[28] Gränacher, *Helv. Chim. Acta.* *3,* 721 (1921).

range 110°–150°. A mixture of fatty acids, from acetic upwards in the series, is produced. Alkaline solutions of these fatty acids are red in color due to the presence of nitro compounds. As might be expected the results of oxidizing with nitric acid and by permanganate are quite different. The fatty acids, with the exception of acetic acid, are almost invariably more readily oxidized than the hydrocarbons and large yields of the former could, therefore, hardly be expected among the reaction products. Prshevalski [29] has shown that the higher normal fatty acids are oxidized by permanganate at two points, i. e., at the carbon atom adjacent to the end methyl group and also at the carbon atom adjacent to the carboxyl group. Isobutyric acid is oxidized to the oxy acid $(CH_3)_2 = \underset{\displaystyle OH}{\underset{|}{C}} — CO_2H$ but with hydrocarbons the molecules are completely broken up. Nitric acid, however, forms a series of fatty acids and dicarboxylic acids. In addition to carbon dioxide and the simpler fatty acids, oxalic, succinic and adipic acids have been observed among the oxidation products.[30] Oxidation by nitric acid may become violent at 100°.[31]

Chromyl chloride, CrO_2Cl_2 has been employed by Etard [32] and by Miller and Rohde [33] to oxidize the aliphatic side chains of benzene derivatives. Toluene yields benzaldehyde and ethyl benzene is oxidized mainly at the CH_2 group to form acetophenone. This interesting reaction, however, has not been applied to the study of the paraffine hydrocarbons, although Etard oxidized hexane to a chloroketone and Schulz [34] treated a number of light fractions from Boryslaw petroleum with chromyl chloride, obtaining ketone mixtures which were not further studied or identified.

Sulfur.

Sulfur reacts with paraffines and naphthenes on heating, hydrogen sulfide being evolved, but little is known regarding the other products formed. Galletly [35] first noted that hydrogen sulfide could conveniently be prepared by heating sulfur and paraffine wax. Somewhat

[29] *J. Chem. Soc. Abs. 1913,* I, 1151.
[30] Markownikow, *Chem. Zentr. 1899,* I, 1064; II, 472, 473; *Ber. 32,* 144 (1899); *J. prakt. Chem.* (2), 59, 556 (1899).
[31] Young & Francis, *J. Chem. Soc. 73,* 928 (1898).
[32] *Compt. rend. 90,* 534 (1880).
[33] *Ber. 23,* 1070 (1890).
[34] *Petr. 6,* 189.
[35] *Chem. News 24,* 107 (1871).

later Lidoff [36] made hydrogen sulfide by passing naphtha vapors into sulfur at 350° to 400°. Friedmann [37] isolated thiocresol as one of the reaction products of sulfur and methylcyclohexane but was unable to isolate benzene from the reaction product of sulfur and hexane. He isolated dinitrobenzene after nitrating the product, which Friedman states is possibly due to the initial formation of cyclohexadiene which on nitration is converted into dinitrobenzene. Guiselin [38] noted that "benzine" dissolves about 0.5% sulfur at 20°, the higher boiling distillates dissolving somewhat more than this. Raffo and Rossi [39] state that pyridine catalyzes the evolution of hydrogen sulfide when hydrocarbons and sulfur are heated. Markownikow [40] obtained xylene from an octonaphthene. Normal hexane [41] is practically inert to sulfur at 210° but paraffine wax or heavy greases react vigorously at this temperature. Prothiere [42] obtained 48 liters of hydrogen sulfide from 70 grams of sulfur and 30 grams of vaseline. It has occasionally been suggested that sulfur might be employed to remove hydrogen from paraffines or petroleum oils to form highly unsaturated oils having several double bonds and such products presumably would have the general character of drying oils. However, since sulfur reacts much more readily with the ethylene bond than it does upon saturated hydrocarbons, the result is a certain amount of carbonized material and unchanged oil or paraffine, a hydrocarbon molecule once being reacted upon then rapidly reacting with more sulfur to form a series of products of unknown character, the final product resembling asphalt, or when strongly heated, petroleum coke. When added to heavy residuum and blown with air, sulfur has the effect of giving a markedly harder so-called asphalt.[43] Sulfur derivatives frequently exhibit a much greater tendency to polymerize than their oxygen analogues and this fact may account for the greater hardness, i. e., greater degree of polymerization, of asphalts made from residuum high in sulfur; for example, that from Mexican petroleum. Under these conditions a large part of the sulfur contained in or added to the original residuum remains in the final product. The following results obtained by blowing a residuum, 12° Bé, from Texas Gulf Coast petroleum, with air are representative.

[36] *Chem. Zentr. 1882*, 22.
[37] *J. Chem. Soc. Abs. 1917*, I, 13.
[38] *Petroleum, 1913*, 1309.
[39] *Gazz. Chim. Ital. 44*, 104 (1914).
[40] *Ber. 1887*, 1850.
[41] Spanier, Dissertation, Karlsruhe, *1910*.
[42] *Chem. Zentr. 1903*, I. 492.
[43] Brooks & Humphrey, *J. Ind. & Eng. Chem.* 8, 746 (1917).

EFFECT OF SULFUR ON HARDNESS OF BLOWN ARTIFICIAL ASPHALT.

	Sulfur added %	Temp. °C	Hours Blown	Penetration mm.*	Flowing-point °C
(1)	None	210	14	Too soft for measurement	
(2)	4.0	210	10	61	73
(3)	6.0	210	10	28	109
(4)	8.0	210	10	17	148
(5)	8.0	215	10	13	167

*Penetration of No. 2 needle, 100 gram weight for 5 seconds at 25°C.

Nitration of Non-Benzenoid Hydrocarbons.

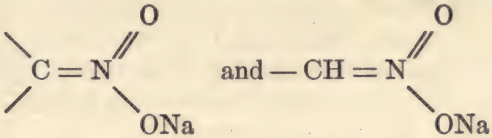
Probably on account of the great industrial importance of nitro derivatives in the aromatic series, the nitration of non-benzenoid hydrocarbons of open chain and cyclic structure has been relatively little investigated. Oxidation by nitric acid generally takes place to a much greater extent in the case of saturated non-benzenoid hydrocarbons than with those of the aromatic series and the relative yields of oxidation and nitration products depend upon many factors, chief of which are the concentration of the nitric acid used and the temperature. The constitution of the hydrocarbon is also of importance. The use of dilute nitric acid, Specific Gravity 1.025 to 1.075, at 115° to 125°, constitutes a method whereby fairly good yields of nitro-derivatives may be obtained. The reaction is usually carried out in sealed tubes in the case of very volatile hydrocarbons, but easily nitrated hydrocarbons are preferably heated with the dilute acid under a reflux condenser. These methods are due chiefly to Konowalow,[44] and to Markownikow.[45] Concentrated or fuming nitric acid or nitric-sulfuric acid nitrating mixture gives mostly oxidation products. Hydrocarbons containing a tertiary hydrogen atom, R_3CH, are most easily nitrated; for example, 2, 5-dimethylhexane yields a dinitro derivative,[46] which is insoluble in alkali solution and which exhibits the exceptional property of being crystalline, melting at 124°–125°.

$$CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3 \longrightarrow CH_3-\underset{\displaystyle NO_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2-\underset{\displaystyle NO_2}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

The hydrocarbon 2, 6-dimethylheptane similarly gives the tertiary nitro derivative, which is easily separated from the relatively small amount of primary and secondary nitro-compounds by the solubility

[44] *Ber.* 25, 1244 (1892) ; 28, 1852 (1895) ; 29, 2199 (1896).
[45] *J. prakt. Chem.* (2) 59, 564 (1899).
[46] Konowalow, *J. Russ. Phys.-Chem. Soc.* 38, I, 109 (1906).

of the latter two classes in aqueous alkali. This solubility in alkali of nitro derivatives of the types $CH.NO_2$ and $-CH_2NO_2$ is a general property common to all nitro derivatives of these types,[47] the alkali salts probably having the constitution represented by the formulae



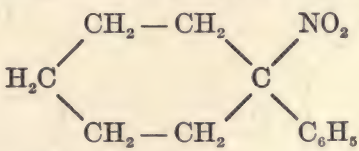
The hydrocarbon 2,7-dimethyloctane yields, with concentrated nitric acid, the primary nitro derivatives, but with dilute acid gives 2,7-dinitro-, 2,7-dimethyloctane, melting point 101.5°–102°.

As contrasted with the above hydrocarbons, containing tertiary hydrogen, the hydrocarbons

$$(CH_3)_3C.CH_2CH_3 \text{ and } (CH_3)_3C.CH_2CH_2CH_3$$

are nitrated only with difficulty; in fact, the former can be purified from isomeric hydrocarbons by repeatedly nitrating the fraction boiling at 48°–51°.[48] When these hydrocarbons are nitrated, the nitro-group is attached to the carbon atom next to the $(CH_3)_3.C$ group. The normal paraffines are also nitrated much less readily than their branch chain isomers. Di-isopropyl $(CH_3)_2CH.CH(CH_3)_2$ reacts very energetically with nitric acid at 20°, but not with the nitric-sulfuric acid nitrating mixture commonly employed to nitrate benzene.

That saturated non-benzenoid hydrocarbons are more easily nitrated by dilute nitric acid than the benzene ring is shown by a number of examples. Phenylcyclohexane is nitrated in the cyclohexane, not in the benzene ring.[49] Here also nitration takes place at the tertiary hydrogen atom yielding 1-nitro-1-phenylcyclohexane



Ortho-xylene with dilute nitric acid, Sp. Gr. 1.075 at 110° gives o-tolylnitromethane,[50] which like all primary nitro compounds easily forms alkali salts. Dilution of nitric acid with acetic acid has practi-

[47] Cf. Nef. "Constitution of the Nitroparaffines." *Ann.* *270,* 331 (1892); *280,* 263 (1894).
[48] Markownikow. *Chem. Zentr.* *1899,* II, 472: *Ber.* *32,* 1446, (1899): *Ber.* *33,* 1908 (1900).
[49] Kursanoff. *J. Chem. Soc. Abs.* *1907,* I, 599.
[50] Konowalow. *J. Chem. Soc. Abs.* *1905,* I, 762.

cally the same effect as dilution with water; dilution and heating directs the nitration chiefly to the side chain, forming nitro derivatives and also acids by oxidation. In accord with the above observations 1.2-diphenylpropane gives the primary nitro derivative rather than substitution in the benzene ring, $C_6H_5CH_2CH(C_6H_5).CH_2NO_2$. Benzoyl nitrate is a reagent, which with benzene, toluene, phenol, anisole, naphthol, coumarine and thiophene gives nitro derivatives very smoothly, but when several methyl groups are present, nitration of a methyl group takes place, as in durene.[51]

$$C_6H_2(CH_3)_4 \longrightarrow C_6H_2(CH_3)_3.CH_2NO_2$$

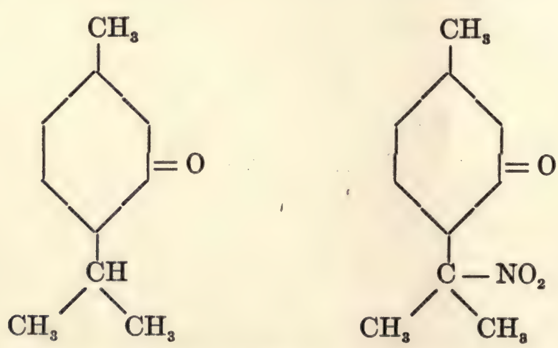
In nitrating p-cymene the isopropyl group is attacked at the tertiary hydrogen atom forming p-methylacetophenone, by oxidation, unless special precautions are taken,[52] advantage being taken of the fact that the paraffines are but little affected by nitric-sulfuric acid nitrating mixture.

The aliphatic ketones are much more reactive to nitric acid than the hydrocarbons. Nitric acid, specific gravity 1.38, yields a mixture of products of which dinitro ketones and dinitro hydrocarbon derivatives are conspicuous, the formation of these products being accompanied by splitting of the carbon structure, probably as indicated by the reaction,

$$\text{(a)}\quad RCO.CH_2R' \longrightarrow RCO.C(NO_2)_2R'$$

$$\text{(b)}\quad R.CO.C(NO_2)_2R' + H_2O \longrightarrow RCOOH + R'CH(NO_2)_2$$

Menthone is readily nitrated by dilute nitric acid to the mononitro derivative[53]



[51] Willstätter & Kubli. *Ber.* *42*, 4152 (1909).
[52] Andrews, *J. Ind. & Eng. Chem.* *10*, 453 (1918).
[53] Konowalow, *Ber.* *26*, Ref. 878 (1893); *28*, Ref. 1054 (1895).

Suflonation

The difference in the ease with which benzenoid hydrocarbons on the one hand and paraffine or non-benzenoid hydrocarbons on the other are sulfonated is not as great as is commonly supposed. Although data with respect to hydrocarbons of known character and purity are extremely meager, Worstall[54] showed that n.hexane, n.heptane, and n.octane are readily sulfonated by fuming sulfuric acid at the temperature of a water bath and Markownikow[55] states that naphthenes also are reacted upon by fuming sulfuric acid, both sulfonation and oxidation taking place. Paraffine wax is attacked by warm fuming sulfuric acid but oxidation rather than sulfonation is the result.[56] Oxidation occurs with fuming acid and saturated hydrocarbons to a much greater extent than in the case of benzene and its derivatives. Hydrocarbons containing a tertiary hydrogen group as in di-isopropyl $(CH_3)_2CH.CH(CH_3)_2$ are much more readily sulfonated and oxidized than normal paraffine hydrocarbons and it is possible that the large losses experienced in the refining of lubricating oils by concentrated sulfuric acid are in part due to the sulfonation and oxidation of branched chain hydrocarbons.

Halides. Preparation and Properties.

In the following pages the methods of preparation and more particularly the properties of the simpler alkyl halides will be discussed. Very little work has been done with fluorine derivatives, and such information as we have does not indicate that fluorine derivatives possess particularly interesting or valuable properties. When writing of the halogen derivatives, it will, therefore, be understood that generally chlorides, bromides or iodides only are meant.

Our knowledge of the simpler alkyl halides, especially chlorides, has recently been much extended by the development of synthetic rubber, and this, it may be noted, is coincident with the production of enormous quantities of electrolytic chlorine at very low cost. Cheap chlorine makes many processes industrially possible, which heretofore have been only of theoretical interest.

The conditions for the chlorination of methane have been noted (page 79). Chlorine reacts readily with butane and pentane and the higher paraffines in the cold and in diffused daylight. It has repeatedly been observed that in chlorinating petroleum ether a sluggish so-called induction period is first noted. The chlorine dissolves in the hydro-

[54] *Am. Chem. J. 23,* 654 (1898).
[55] *J. Russ. Phys.-Chem. Soc. 1892,* 141.
[56] Michailescu & Istrati. *Bull. Soc. Sci. Bucharest.* 13, 143.

carbon apparently without reacting, but, after a few minutes, the color is suddenly discharged and the reaction thereafter proceeds very rapidly. An excellent example of this peculiar induction period [57] has been observed in the case of brominating cyclohexanone and 1, 1-dimethylhexanone (3). Catalysts are not necessary, although the presence of moisture is distinctly advantageous in the case of the more volatile hydrocarbons.[58] The chlorination of petroleum pentane has become of industrial importance in connection with the manufacture of synthetic amyl acetate (see page 89). In order to produce mainly monochlorides, it is necessary to stop the chlorination after the concentration of monochlorides in the reaction mixture has reached about 20 per cent, and separate the unchanged pentane by fractional distillation. The relative proportions of the isomeric monochlorpentanes formed are not known. Cyclohexane is more reactive to halogens than n.hexane. When n.hexane is chlorinated, the CH_2 groups, not the CH_3 groups, are attacked.[59]

The chlorination of paraffine wax is carried out industrially, the product being used as a solvent for dichloramine — T.[60] Boiling the product with aniline readily removes most of the chlorine. The higher boiling petroleum fractions, are readily chlorinated in diffused daylight at ordinary temperature, but the products are very unstable.

Bromine reacts more slowly with the paraffines. Pentanes may be brominated readily under the influence of intense illumination, and the higher paraffines react readily with bromine when gently warmed and illuminated. In the presence of metallic iron or ferric bromide, bromine readily forms a series of substitution products in which one bromine atom is attached to each carbon atom, thus

$$CH_3CH_2CH_2CH_2CH_3 \longrightarrow CH_2Br.CHBr.CHBr.CHBr.CH_2Br.$$

Normal heptane and an excess of bromine in the presence of iron yields 1, 2, 3, 4, 5, 6, 7-heptabromoheptane. Ethyl bromide may be brominated under these conditions to ethylene bromide and propyl bromide to 1.2-dibromopropane.[61] Bromides have been made by treating chlorine derivatives, such as CCl_4, C_2Cl_4 and C_2Cl_6, with anhydrous aluminum bromide.[62]

Sodium iodide reacts with many alkyl chlorides and bromides to

[57] Crossley & Renouf. *J. Chem. Soc. 91,* 81 (1907).
[58] Aschan, *Chem. Abs. 1919,* 2868.
[59] *Ber. 39,* 2138 (1906); Strauss claims to be able to prepare primary monochlorides by chlorinating at reduced pressures and temperatures above the boiling-point of the hydrocarbons. (German Pat. 267, 204.)
[60] Dakin & Dunham, *Brit. Med. J. 1918,* I, 51.
[61] V. Meyer & Müller, *J. prakt. Chem.* (2) *46,* 171 (1892).
[62] Gustavson, *Chem. Zentr. 1881,* 131,642.

give the corresponding alkyl iodide and sodium chloride or bromide. Sodium iodide dissolves readily in acetone and this solvent yields the best results in carrying out the reaction, which usually takes place at once at ordinary temperatures, with the separation of sodium chloride or bromide.[63]

Unsaturated substances may be brominated without affecting the double bond, substitution taking place, by employing N-bromo-acetamide. Thus

$$(CH_3)_2C = C(CH_3)_2 \text{ yields } (CH_3)_2C = C(CH_3)\ CH_2Br.$$

Sodium hypobromite, although a very energetic oxidizing agent, converts acetone into carbon tetrabromide (and acetic acid). Bromoform also yields carbon tetrabromide with this reagent.[64]

In the great majority of cases, it is much preferable to prepare alkyl halides from an alcohol or olefine than by treating the hydrocarbons themselves with chlorine or bromine, the latter method giving mixtures of isomeric derivatives. Since it is usually possible to obtain the simpler aliphatic alcohols in a state of purity, they constitute a valuable raw material for the preparation of pure mono-halides. The methods employed will only be mentioned and reference made to original articles or works on preparative methods for further data.[65]

(1) Hydrochloric acid gas, and methyl or ethyl alcohol in the presence of zinc chloride gives good yields of the corresponding chlorides, but this method is practically valueless with the higher alcohols on account of the instability of the higher alkyl chlorides in the presence of zinc chloride. Tars or heavy polymers are formed with the higher alcohols. However, Norris[66] has obtained good yields from a large number of alcohols by using a large excess of concentrated hydrochloric acid, without zinc chloride.

(2) Hydrobromic acid and hydriodic acid give very much better yields, than hydrochloric acid. With the simpler alcohols the well-known sulfuric acid and sodium bromide method gives excellent results, but not with the higher alcohols. In the case of the higher alcohols much better results are obtained by the method of Norris,[66] in which the alcohol is gently heated with the concentrated aqueous acid

[63] Finkelstein, *Ber.* *43*, 1528 (1910).
[64] Dehn, *J. Am. Chem. Soc.* *31*, 1220 (1909).
[65] Weyl, *Methoden d. Org. Chem.* II. 1077.
[66] Norris, Watt & Thomas, *J. Am. Chem. Soc.* *38*, 1071 (1916). Norris & Mulliken: *J. Am. Chem. Soc.* *42*, 2093 (1920). According to the author's experience, the halides prepared according to this method are purer and much preferable to similar products made by other methods. Particularly is this true when the halides are to be employed in a Grignard reaction. According to German Patent 280,740 the addition of calcium chloride is advantageous.

and the alkyl halide removed as formed by distillation from the mixture. This method gives especially good yields with tertiary amyl alcohol, tertiary butyl alcohol, octyl alcohol, cetyl alcohol, etc. By the Norris method good yields are obtainable in many cases with concentrated hydrochloric acid. In this connection it is of interest to note that the glycol $S(CH_2CH_2OH)_2$ gives the dichloride quantitatively with concentrated aqueous hydrochloric acid at 60°.[67] Tertiary alcohols of the type $ROCH_2C(OH)R_2$ give excellent yields of the chloride on warming with 38% hydrochloric acid.[68]

(3) The use of PCl_3, PCl_5 and PBr_3 in preparing alkyl chlorides and bromides is well known, but the yields are greatly reduced by the formation of esters of phosphorus or phosphoric acid. Iodides are commonly made by introducing iodine into a mixture of the alcohol and red phosphorus which method has been recently improved for the simpler alkyl iodides by Adams and Voorhees.[69] Dehn and Davis[70] state that yields of 85 and 88 per cent of isobutyl and iso-amyl chlorides respectively can be obtained from the corresponding alcohols by adding PCl_3 to a mixture of the alcohol with concentrated aqueous zinc chloride. In the case of tertiary alcohols, acetyl chloride frequently reacts abnormally, giving the corresponding chlorides instead of the acetates, for example, dimethylbutylcarbinol thus yields the corresponding chloride.

(4) It is well known that olefines combine with halogen acids to form alkyl halides. In the case of hydrocarbons, generally the halogen will combine with that carbon atom of the olefine group which has combined with it the least number of hydrogen atoms, which generalization is known as Markownikow's rule:

$$CH_3CH = CH_2 \longrightarrow CH_3CHI.CH_3$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH_2 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\displaystyle Br}{\underset{|}{C}} - CH_3$$

However, small quantities of the isomeric halides are sometimes formed. Thus propylene yields very small quantities of n.propyl

[67] H. T. Clarke, *J. Chem. Soc. 101,* 1583 (1913). Gomberg, *J. Am. Chem. Soc. 41,* 1415 (1919). This chloride is the now well known "Mustard Gas."

[68] Paloma, *Chem. Abs. 1919,* 2862.

[69] *J. Am. Chem. Soc. 41,* 789 (1919).

[70] *J. Am. Chem. Soc. 29,* 1328 (1907) ; When PCl_3 reacts with an alcohol, successive formation and decomposition of the whole series of possible alkyl phosphites results, and the series of reactions may be arrested by choosing the experimental conditions to get very large yields of $P(OR)_3$, $P(OR)_2.OH$, $P(OR).(OH)_2$ or $P(OH)_3$ and 3 RCl. [Milobendzki and Sachnowski, *J. Chem. Soc. Abs. 1918,* I. 477.]

iodide,[71] and isobutylene yields, with a solution of HBr in acetic acid, about 93 per cent tertiary butyl bromide and 7 per cent isobutyl bromide.[72] Acetic acid solutions of hydrogen chloride and bromide have given particularly good results in the terpene and sesquiterpene series, where crystalline hydrochlorides are often difficult to obtain.[73]

The ability of an olefine to combine with halogen acid depends somewhat upon its structure. Thus trimethylethylene

$$\begin{array}{l} CH_3 \\ \quad >C=CH.CH_3 \\ CH_3 \end{array}$$

combines readily with hydrogen chloride, but the isomeric amylenes do not. Advantage of this fact is taken in one of the synthetic rubber processes,[74] in which normal pentane is chlorinated to a mixture of monochlorides. The monochlorides are converted into amylenes by passing over quicklime at 385° to 400° and the resulting amylene vapors are passed over alumina at 450°. The amylene fraction boiling from 34° to 38° contains trimethylethylene, which is removed by combining with hydrogen chloride and the tertiary amyl chloride, boiling point 84° to 86°, isolated by fractional distillation.

Unstable carbon ring structures are often ruptured by halogen acids. Pinene in acetic acid solution gives mainly dipentene dihydrochloride, with rupture of the bridged or cyclobutane ring.

Bromocyclopropane[75] and bromocyclobutane[76] and cyclopropyl carboxylic acid are converted into open chain compounds by concentrated hydrobromic acid. Thus

$$\begin{array}{l} CH_2 \\ | \quad >CHBr + HBr \longrightarrow CH_3CHBr.CH_2Br. \\ CH_2 \end{array}$$

$$\begin{array}{l} CH_2 \\ | \quad >CH.CO_2H + HBr \longrightarrow CH_2Br.CH_2CH_2CO_2H \\ CH_2 \end{array}$$

$$\begin{array}{lcl} \quad\quad Br:H & & \\ \quad\quad\quad : & & \\ CH_2 \text{———} :\text{–}CH_2 & & CH_2Br \quad CH_3 \\ | \quad\quad\quad\quad : \ | & \longrightarrow & | \quad\quad\quad\quad | \\ CH_2 \text{————} CHBr & & CH_2 \text{——} CHBr \end{array}$$

[71] Michael & Leighton, *J. prakt. Chem.* **60**, 348, 446 (1899).
[72] Ipatiev & Ogonowsky, *Ber.* **36**, 1988 (1903).
[73] For good results, the reaction mixture saturated with HCl or HBr should be allowed to stand two or three days in a cool, dark place.
[74] Badische A. & S. Fab. *Brit. Pat.* 18, 356 (1911).
[75] Willstätter & Bruce, *Ber.* **40**, 4457 (1907).
[76] Perkin, *J. Chem. Soc.* **65**, 950 (1894).

It will be noted in the last case that the bromine atom of the HBr molecule combines in such a way as to place it in the position farthest removed from the bromine atom already present in the ring. This illustrates the positive-negative rule of Michael,[77] which is not as empirical as Markownikow's rule. According to Michael's principle the combination of two molecules, for example, halogen acid and an olefine, tends to occur with such structural results as will give the maximum degree of entropy, that is the neutralization of the chemical energies or affinities of the reacting atoms. This generalization is, therefore, a special case of Ostwald's hypothesis that "every system tends towards that state whereby the maximum entropy is reached.[78]

Michael formulated his principle after a comprehensive study of addition reactions. The marked influence of a methyl group is shown in the formation of $CH_3CHBr.CH_3$ from propylene, $CH_3CBr_2CH_3$ from $CH_3CBr = CH_2$, $CH_2Br.CH_2.CO_2H$ the chief product of HBr and $CH_2 = CH.CO_2H$, etc. The rule is not without many exceptions, however. Faworsky [79] considers the matter from the standpoint of relative reaction velocities. By heating isopropyl bromide to 250° several times, removing the fraction boiling at 69°–70° each time he was able to effect 20 per cent conversion of isopropyl bromide to normal propyl bromide. The conversion of normal propyl bromide to isopropyl bromide is therefore reversible and the addition of HBr to propylene takes place in part contrary to Markownikow's rule and Michael's principle, the result being dependent upon the relative velocities of the two reactions.

(1) $CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBr.CH_3$ (main result).

(2) $CH_3CH = CH_2 + HBr \longrightarrow CH_3CH_2CH_2Br$

Similar reversible relations were found in the bromopentane series. Faworsky confirmed the earlier observation of Eltekow that isobutyl and tertiary butyl bromides are in equilibrium at about 210°, as noted in the following:

$$(CH_3)_3CBr \leftrightarrows HBr + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH_2 \rightleftarrows \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CHCH_2Br.$$

In a similar manner it was shown that ethylidene bromide is present in the mixture resulting from heating ethylene bromide:

[77] *J. prakt. Chem. 46,* 205 (1892).
[78] *J. prakt. Chem. 60,* 286, 292 (1899); *Ber. 39,* 2138 (1906).
[79] *Ann. 354,* 325 (1907).

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} \leftrightarrows \begin{array}{l} CHBr \\ \| \\ CH_2 \end{array} + HBr \rightleftarrows CH_3CHBr_2$$

Hydrogen bromide combines with $CH_2 = CH.CH_2Br$ in the light to form trimethylene bromide, $CH_2Br.CH_2CH_2Br$ quantitatively, but in the dark considerable propylene bromide is formed.[80]

General Properties of the Simpler Alkyl Halides: One of the most conspicuous properties of the alkyl halides is the relative ease with which they are decomposed by heat to form olefines and halogen acid. Accurate data are practically confined to the simpler substances. The decomposition of the two propyl bromides was studied by Aronstein.[81]

PER CENT DISSOCIATION BY HEAT.

Temperature	*n.Propyl Bromide*	*Isopropylbromide*
113°	....	5.40
138°	....	7.30
180°	2.9	15.10
210°	10.4	21.00
262°	31.9	56.00

Roozeboom [82] has determined similar values for the decomposition of *tertiary* butyl bromide to isobutylene and HBr.[83]

Temperature	*Per Cent Dissociation*
115°	4.2
130°	10.0
150°	26.0
183°	42.6
204°	60.0
250°	76.0
300°	85.2

Chlorine and bromine derivatives of petroleum fractions, kerosene fractions for example, are very unstable, and as, noted by Markownikow [84] and others, decompose slowly at ordinary temperatures with liberation of halogen acid. When such chlorine or bromine derivatives are treated with sodium iodide in acetone free iodine is liberated. The decomposition of these halides is probably accelerated by light.[85] Kipping and Davies attribute the instability of chlorinated petroleum oils to compounds of the type R_3CX.

The dissociation of alkyl halides, particularly in the presence of

[80] Holleman & Matthes, *Chem. Abs. 1918,* 2545.
[81] *Rec. trav. chim. 1,* 134 (1882).
[82] *Ber. 14,* 2396 (1881).
[83] The decomposition of amyl bromides by heat has recently been investigated by Colson, *Compt. rend. 1918,* 1548.
[84] *Ann. 301,* 185 (1898).
[85] Pfeiffer, *Z. angew. Chem. 1913,* 545, noted the decomposition of nitro stilbene dichloride by light.

aluminum chloride, is intimately associated with the subject of the rearrangements which alkyl halides and olefines undergo. Thus Freund [86] showed that isobutyl halides were partially converted into tertiary derivatives on heating with aluminum chloride in sealed tubes,[87] and the formation of *tertiary* butyl derivatives of benzol toluene and xylene by condensing *isobutyl* chloride or bromide with these hydrocarbons according to Friedel and Crafts' method has been well established by Baur.[88] Nef has advanced two explanations of such rearrangements. In his earlier work he supposed the intermediate formation of a nascent olefine. According to this theory the formation of tertiary butyl ethyl ether from isobutyl iodide and alcoholic silver nitrate is as follows:

$$\text{(a)}\qquad \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CHCH_2Br \longrightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\underset{|}{C}-\underset{|}{CH_2}$$

$$\text{(b)}\qquad \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\underset{|}{C}-\underset{|}{CH_2}+C_2H_5OH \longrightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\underset{\underset{OC_2H_5}{|}}{C}-CH_3$$

In a similar manner isobutyl iodide and silver cyanate yield a mixture of about two parts tertiary butyl isocyanate and one part of the isobutyl derivative; silver acetate in acetic acid yields about two parts tertiary butyl acetate to one part isobutyl acetate.[89] Wischnegradsky showed that secondary iso-amyl alcohol with halogen acids yields chiefly the tertiary halide.[90]

$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>CH\underset{\underset{OH}{|}}{CH}.CH_3 \longrightarrow \begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\underset{\underset{X}{|}}{C}.CH_2CH_3$$

Also the secondary halide, when heated with lead hydroxide, yields the *tertiary* alcohol.

But the facts are somewhat more involved than is indicated above. Thus isobutyl alcohol, when decomposed by heat, and the primary isobutyl halides with alcoholic alkali gives a mixture of butylenes

[86] *J. prakt. chem.* (2), *12*, 26 (1875).

[87] The nature of the decomposition products of alkyl halides in the presence of anhydrous aluminum chloride, either alone or in the presence of saturated or unsaturated non-benzenoid hydrocarbons, has never been carefully investigated. Cf. Meyer, *Ber.* *27*, 2766 (1894).

[88] *Ber.* *24*, 2832 (1891); *31*, 1344 (1898); *32*, 3647 (1899). Nitrated tertiary butyltoluene and xylene are known commercially under the name of artificial musk.

[89] Butlerow, *Ann.* *168*, 143 (1873); Nef, *Ann.* 309,150 (1899).

[90] *Ann.* *190*, 342 (1878).

which have been shown to contain isobutylene and α and β-normal butylenes.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH.CH_2X \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!C = CH_2 \qquad \text{and}$$

$$\begin{matrix} CH_3CH = CH.CH_3 \\ CH_3CH_2CH = CH_2 \end{matrix} \qquad \text{and}$$

Nef believed that such facts could best be explained by the intermediate formation of a cyclopropane ring, which structure is known to be ruptured easily. Thus

$$\begin{array}{l} CH_3 - CH - CH_2X \\ \qquad\;\, | \\ \qquad CH_2H \end{array} \rightarrow \begin{array}{l} CH_3 - CH - CH< \\ \qquad\;\, | \\ \qquad CH_2H \end{array} \rightarrow$$

$$\begin{array}{c} CH_3 - CH - CH_2 \\ \diagdown\;\diagup \\ CH_2 \end{array} \rightarrow \begin{array}{l} CH_3 - CH - CH_2 - CH_2 \\ \qquad\;\;\, | \qquad\qquad\;\, | \end{array} \rightarrow \begin{array}{l} CH_3CH = CHCH_3 \\ CH_3CH_2CH = CH_2 \end{array}$$

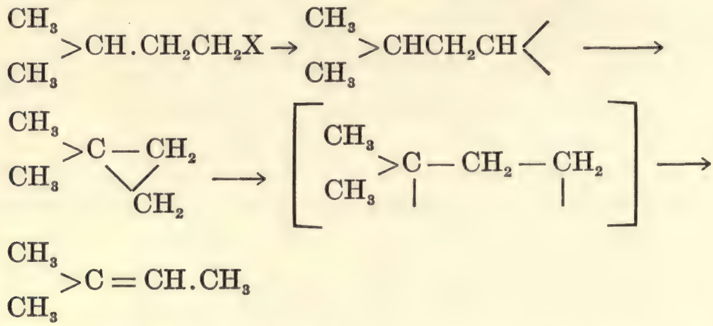
$$\text{(a)} \qquad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CHCH_2Br \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\begin{array}{l} C - CH_2 \\ | \qquad | \end{array}$$

$$\text{(b)} \qquad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\begin{array}{l} C - CH_2 \\ | \qquad | \end{array} + C_2H_5OH \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\begin{array}{l} C - CH_3 \\ | \\ OC_2H_5 \end{array}$$

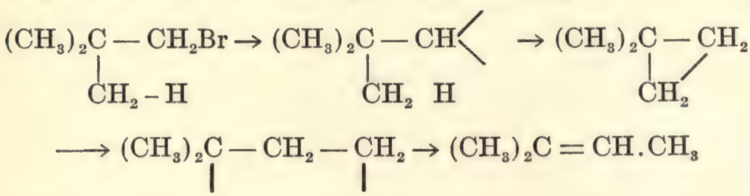
The reaction of the solvent is frequently important in such reactions. Isobutyl iodide and silver acetate give a small yield of about equal parts of isobutyl acetate and tertiary butyl acetate. Tertiary butyl iodide, however, does not give the acetate except when acetic acid is employed as a solvent. It is significant also that tertiary butyl iodide gives only isobutylene when treated with silver cyanide, oxide or cyanate, nothing resembling a so-called double decomposition reaction taking place. Tertiary butyl iodide and silver nitrate in alcohol solution gives no trace of tertiary butyl nitrate; nitric acid is not known to react with a double bond to give an alkyl nitrate, in the same manner that sulfuric acid yields alkyl sulfuric esters.[92]

[92] Nef, *loc. cit.*

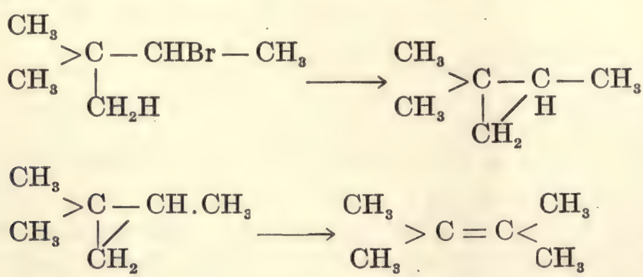
In the amylene series several cases of rearrangement have been well established which are capable of a similar explanation. Thus primary iso-amyl alcohol and the corresponding halides yield chiefly trimethyl ethylene;



The formation of this olefine from bromotetramethylmethane, observed by Tissier [93] may be similarly explained without resorting to the vague idea of the "wandering" of the methyl group.



Another rearrangement involving a change in the position of a methyl group is that noted by Coutourier.[94]



Some support for Nef's theory of such changes is found in the properties of the cyclopropane ring (see page 77).

The mechanism of dissociation of the alkyl halides and their so-

[93] *Ann. chim. phys.* (6), *29*, 361 (1893).
[94] *Ann. chim. phys.* (6), *26*, 464 (1892).

called double decomposition reactions is of fundamental importance. Nef[95] has advanced the theory, which he has developed from his previous studies of bivalent carbon, that alkylidene dissociation first occurs.

$$\text{(a)} \qquad RCH_2CH_2X \longrightarrow RCH_2CH< + HX$$

$$\text{(b)} \qquad RCH_2CH< \longrightarrow RCH=CH_2$$

Whether or not olefines are found in the reaction products depends upon the presence or absence of substances capable of reacting with the very reactive alkylidene, the rate of this reaction as compared with the rate of the rearrangement to the olefine, and other secondary factors. Thus Nef explains the apparently contradictory results obtained by previous investigators by showing that when ethyl chloride is decomposed by heating to 550° and the gases subsequently passed over soda lime to remove the hydrogen chloride, a nearly quantitative yield of ethylene was obtained. If, however, ethyl chloride is passed directly into hot soda lime at 550° ethyl alcohol or rather the decomposition products of ethyl alcohol under these conditions, acetate, carbonates, methane and hydrogen, are obtained. Hydrogen chloride acting upon the soda-lime liberates water, which may then react with the labile, reactive alkylidene as follows:

$$\text{(a)} \qquad CH_3CH< + HOH \longrightarrow CH_3CH<^{OH}_{H}$$

$$\text{(b)} \qquad CH_3CH< + H_2O \longrightarrow CH_3CHO + H_2$$

The behavior of the simpler alkyl halides to *alcoholic alkali* has been thoroughly investigated by Nef, with the results summarized below:

Halide	Olefine %	Ether %	Temp. °C.	
C_2H_5Br	11.	60. –70.	70 ± 5	
C_2H_5I	14.	60.	40– 90	
$CH_3CH_2CH_2Br$	20.	60.	80–100	
$CH_3CH_2CH_2I$	36.4	40.	80–100	
$CH_3CHBr.CH_3$	75.0	17.	80–100	
$CH_3CHI.C_2H$	93.6	0.?	80–100	
$(CH_3)_2CHCH_2Cl$	....	37.	120	Sodium isobutylate used
"	....	38.5	170	Sodium isobutylate used
$(CH_3)_2CHCH_2Br$	64.	23.	90–100	
$(CH_3)_2CHCH_2I$	98.	0.	90–100	
$(CH_3)_2C<^{CH_3}_{Cl}$	97.	0.	90–100	

[95] *Ann.* *309*, 128 (1899); *318*, 3 (1901).

Halide	Olefine %	Ether %	Temp. °C.
$(CH_3)_2C<\begin{smallmatrix}CH_3\\ I\end{smallmatrix}$	97.	0.	90–100
$(CH_3)_2CH.CH_2CH_2Br$	....	70.5	90–100
$(CH_3)_2CH.CH_2CH_2I$	....	51.	90–100
$(CH_3)_2C<\begin{smallmatrix}C_2H_5\\ Br\end{smallmatrix}$	80.	?	50–60

$CH_2Br.CH_2Br \rightarrow$ vinyl bromide, quantitative.

Vaubel[96] has shown that allyl halides give chiefly allyl ether with alcoholic alkali under a wide variety of conditions. (For the influence of double bonds upon the reactivity of adjacent halogen atoms see page 000.) Nef[97] has also shown that the alkyl sulfates, ethyl, n. propyl, isobutyl and iso-amyl, react with alcoholic caustic potash to give mainly the ethers ROC_2H_5. On heating the alkyl halides with water, alcohols and olefines are formed. The employment of high pressures during the hydrolysis greatly increases the yield of alcohols from chloropentanes.[98]

Acetates are formed when the alkyl halides are heated with an acetate of sodium, potassium, silver or lead and the best results appear to be obtained in glacial acetic acid under pressure. As with ether formation noted by Nef the best yields of alkyl acetates are obtained from the alkyl chlorides, iodides giving the poorest yields. This well-known method is of general application. It is applied industrially in the manufacture of artificial amyl acetate and also in the terpene series in the conversion of bornyl chloride into the acetates of borneol and isoborneol.[99]

The alkyl halides and metallic nitrates give very small yields of alkyl nitrates. Thus Bertrand,[100] with methyl, ethyl and propyl iodides and silver nitrate obtained free nitric acid, and small quantities of ethers and alkyl nitrates. Tertiary butyl iodide and alcoholic silver nitrate yield isobutylene and tertiary butyl ethyl ether in about equal amounts.[101] Ethylene bromide and alcoholic silver nitrate gives a trace only of the dinitrate, a little free nitric acid, some glycoldiethyl ether and the chief reaction product is the ethyl ether mononitrate

$$\begin{array}{l}CH_2OC_2H_5\\ |\\ CH_2ONO_2\end{array}$$

[96] *Ber. 24*, 1685 (1891).
[97] *Ann. 318*, 3 (1901).
[98] Essex, Hibbert & Brooks, *J. Am. Chem. Soc. 38*, 1369 (1916).
[99] Camphene is the principal reaction product.
[100] *Bull. Soc. Chim. 33*, 566 (1881).
[101] Nef, *Ann. 309*, 150 (1899).

Alkyl halides, particularly chlorides, can be converted into the corresponding alcohols by heating with alkali formate in methyl alcohol solution. Henry [102] first noted the ease with which certain alkyl formates react with methyl alcohol to give methyl formate and an alcohol. Nef prepared acetol in this manner and excellent yields of ethylene-glycol can be obtained from ethylene chloride.[103]

(1) $RCH_2Cl + NaO_2CH \longrightarrow RCH_2O_2CH$ (alkyl formate)

(2) $RCH_2O_2CH + CH_3OH \longrightarrow RCH_2OH + CH_3O_2CH + NaCl$

There is no appreciable difference in the behavior of alkyl and non-benzenoid cyclic halides toward magnesium and in the various applications of the Grignard reaction. To cite a few examples among many, Borsche used the Grignard synthesis of sulfinic acids to convert cyclopentyl bromide into cyclopentanesulfinic acid,[104] and Bouveault used bromocyclohexane in the preparation of cyclohexanol.[105] Hesse has patented the conversion of bornyl chloride to borneol by the use of the Grignard reaction,[106] but in this case, as with the higher alkyl halides, the yields are very poor. Bromocyclohexane, like normal and iso-hexane monobromides, is unstable. Alcoholic caustic potash yields mainly cyclohexene.

[102] *Bull. acad. roy. belg.* *1902*, 445.
[103] Brooks & Humphrey, *J. Ind. & Eng. Chem.* 9, 750 (1917).
[104] *Ber.* *40*, 2220 (1907).
[105] *Bull. soc. chim.* (3), *29*, 1049 (1903).
[106] U. S. Pat. 826,165; 826,166.

Chapter III. The Paraffine Hydrocarbons.

Methane.

Methane is described in a special section on account of its commercial importance. One liter of methane (made by the action of water on magnesium-methyl iodide) weighs 0.7168 grams at 0° and 760 mm. pressure.[1] Its melting-point is — 184°.[2] Its boiling-point under 760 mm. pressure is — 164°.[3] The critical temperature is — 82.85°, the critical pressure 45.60 atmospheres, and the critical density 0.1623.[4] The coefficients of expansion x 10^6 are A = 3687 and B = 3681.[5]

The liquefaction of methane has recently become of industrial importance in connection with the separation of helium from natural gas. Pure methane may be separated from ethane and other hydrocarbons in this manner, which is a matter of some importance in the industrial chlorination of methane. Although both the Linde and Claude processes have been employed on a large scale for this purpose, little technical information has been published. Satterly and Patterson[6] have determined the latent heat of vaporization of methane to be 130 calories per gram and ethane 260 calories per gram. Satterly[7] has shown that nitrogen dissolves in liquid methane at moderate pressures and McTaggart and Edwards[8] have determined the temperature and composition relations in the liquid and gas phases in the system methane-nitrogen.

The flame of methane is not very luminous. When burned in an Argand burner at the rate of one cubic foot per hour it gives a flame of 5.2 candle power. Pure methane on combustion yields 1003 B.T.U.

[1] Guye, *Chem. Zentr.* 1909 I. 977.
[2] Baume & Perrot, *compt. rend.* 148, 39 (1909) ; also Wahl, *Proc. Roy. Soc.* *87A*, 371.
[3] Moissan & Chavanne, *Compt. rend.* *140*, 407 (1905) ; Olszewski, *Compt. rend.* *100*, 940 (1885).
[4] Cardoso, *Arch. sci. phys. nat.* *36*, 97, *39*, 400.
[5] Leduc, *Compt. rend.* *148*, 173 (1909).
[6] *Trans. Roy. Soc. Canada.* *13*, 123 (1919).
[7] Ibid., *13*, 109 (1919).
[8] Ibid., *13*, 57 (1919).

per cubic foot.[9] Values for natural gas vary from 950 to about 1250 B.T.U. per cubic foot.

Methane has no physiological effect on men or animals except when present in sufficient per cent to produce the characteristic symptoms of oxygen deficiency. Mine gas and other mixtures of methane and air may, therefore, contain sufficient methane to form explosive mixtures and yet cause no physiological symptoms which might serve as a warning to miners. Haber [10] has developed an interesting automatic warning whistle.

The largest explosive limits for methane and air are those determined by Burrell and Oberfell, i. e., a minimum methane content of 4.9 per cent and a maximum of 15 to 15.4 per cent.[11] Initial pressures of 5 atmospheres do not appreciably effect these ratios, so that these values are practically independent of ordinary variations of barometric pressure. Burgess and Wheeler,[12] and Wheeler [13] find somewhat narrower limits.[14] Wheeler [15] also finds that moderate changes of pressure have only very slight effects on the explosion limits. Coward, Carpenter and Payman,[16] give 5.6 per cent methane as the lower limit of explosibility. Methane and oxygen ignite at 667° and although this ignition point is somewhat lowered by certain metals, oxidation in the presence of palladium is not appreciable below 404°.[17] This fact makes possible the quantitative determination of hydrogen in the presence of methane by selective combustion.[18]

[9] Richards, "Metallurgical Calculations," 1918, p. 25, gives 970 B. T. U. per cubic foot as the net heat of combustion of methane: ethane 1719 B. T. U. and propane 2464 B. T. U. per cubic foot.

[10] (The U. S. Bureau of Mines has recently demonstrated a highly efficient system of warning miners of danger by introducing butyl mercaptan in the air supply.) The Haber apparatus for the detection of methane in mine gases gives warning as the percentage of methane approaches the limit of explosibility. It is based on the principle that differences in the density of a gas are indicated by differences in the sound produced by blowing a whistle or pipe with the gas. The apparatus contains two stopped pipes, which are tuned to the same pitch when filled with the same gas. When one whistle is supplied, by piped connections, with a mixture of methane and air in the proportions corresponding to the lower explosive limit, and the other supplied with the mine air, then the simultaneous blowing of the two whistles produces a beat whose interval diminishes as the pitch of the two pipes approach the same value, or as the mine gas approaches the dangerous composition gas in methane content. When near the explosion limit the beat produces a characteristic shrill sound. Cf. *Chem. Ztg.* *37*, 1329 (1913).

[11] U. S. Bureau of Mines. Techn. Paper *119* and *121* (1916).

[12] *J. Chem. Soc.* *105*, 2591 (1914).

[13] *J. Chem. Soc.* *105*, 2606 (1914); also Mason & Wheeler, *J. Chem. Soc.* *113*, 45 (1918).

[14] Mixtures of methane and air containing 9.6 per cent methane are the most flammable, and the rate of flame travel and explosion violence is greatest with mixtures of this composition. Methane and oxygen, in molecular proportions, gives a flame velocity of 7,616 feet per second. Mason & Wheeler [*J. Chem. Soc.* *117*, 1227 (1920)] give 5.4 per cent as the lower limit of methane and air mixtures for horizontal flame propagation.

[15] *J. Chem. Soc.* *111*, 411 (1917).

[16] *J. Chem. Soc.* *115*, 28 (1919).

[17] Denham, *J. Soc. Chem. Ind.* *24*, 1202 (1905); Phillips, *Am. Chem. J.* *16*, 163 (1894).

[18] Hempel, *Z. anal. Chem.* *31*, 445 (1902); Richardt, *Chem. Zentr.* *1904*, II. 364.

The mechanism of the combustion of methane and other hydrocarbons has been studied by Bone and Wheeler [19] who found that formaldehyde is an intermediate product. Formaldehyde is then further oxidized, with the possible intermediate production of formic acid, to water and carbon dioxide. They represent the combustion of methane as passing through the stages indicated in the following:

$$(1) \quad CH_4 + O_2 \longrightarrow H_2CO + H_2O$$

$$(2) \quad 2H_2CO + O_2 \longrightarrow 2OC{<}\begin{matrix}OH\\H\end{matrix}$$

$$(3) \quad OC{<}\begin{matrix}OH\\H\end{matrix} \longrightarrow H_2O + CO$$

$$(4) \quad 2CO + O_2 \longrightarrow 2CO_2$$

Methane is exceptionally stable to heat. Bone and Coward [20] have shown that its decomposition at 700° is not appreciable, but at slightly higher temperatures it is decomposed directly into carbon and hydrogen without the formation of ethylene or acetylene. Coward and Wilson [21] showed that at 850° the equilibrium mixture contains 97.5 per cent hydrogen and 2.5 per cent methane. At 1000° the equilibrium mixture consists of 1.1 per cent methane and 98.9 per cent hydrogen. At 1200° Pring and Fairlie [22] found a gas mixture in equilibrium with amorphous carbon containing 0.36 per cent methane. The carbon formed by decomposing methane in hot tubes, hot furnace checker work and the like is not a good commercial black but is gray-black in color and usually gritty. Whitaker and Alexander [23] have called attention to the fact that in gas mixtures produced by the thermal decomposition of hydrocarbons, equilibrium corresponding to the temperature employed is rarely, if ever, attained. The composition of the gas is not only dependent upon the temperature to which the mixture is subjected, but is also markedly affected by the time of heating, the pressure and the presence or absence of substances which may catalytically influence the tendency to establish equilibrium.

When methane is decomposed in contact with metals, metallic carbides are sometimes formed; in fact, it has been proposed to intro-

[19] *J. Chem. Soc.* *81,* 541 (1902); *83,* 1074 (1903); Cf. Armstrong, *J. Chem. Soc.* *83,* 1088 (1903).
[20] *J. Chem. Soc.* *93,* 1197 (1908).
[21] *J. Chem. Soc.* *115,* 1380 (1919).
[22] *J. Chem. Soc.* *101,* 91 (1911); Bone & Jordan, *J. Chem. Soc.* *71,* 41 (1897); *79,* 1042 (1901).
[23] *J. Ind. & Eng. Chem.* *6,* 383 (1914).

duce carbon into molten iron in this manner. Magnesium carbide is rapidly formed by heating the metal with methane at 760°. Manganese also readily forms a carbide when heated to 800° in methane.[24]

Chlorination of Methane: The industrial production of carbon tetrachloride, methyl chloride, chloroform and dichloromethane from methane or natural gas, is peculiarly an American opportunity on account of the availability of natural gas. No process for the manufacture of methane, as by the hydrogenation of carbon monoxide, has as yet been operated on an industrial scale. The problem of manufacturing these chlorinated derivatives is an old one but recent interest in this direction is coincident with the steadily increasing value of the products of wood distillation, particularly methyl alcohol and acetone, and the rapid development of the electrolytic chlorine industry and relatively cheap liquid chlorine. Obviously, the maximum economic advantage would be secured by bringing natural gas and electrolytic chlorine production together. As pointed out elsewhere, natural gas varies considerably in the proportions of methane and other hydrocarbons, but so-called dry gases containing very low percentages of ethane and higher methane homologues are widely distributed. According to reported analyses [25] such dry gas is available at numerous localities in the Louisiana, Texas and California fields and, as has already been pointed out, pure methane can be separated from its homologues by liquefaction methods so that West Virginia or other gas could thus be employed.

Chlorine and methane do not react in the dark at ordinary temperatures but Bedford [26] states that fairly good yields of methyl chloride and carbon tetrachloride may be obtained, without explosions, by chlorinating at 0° in strongly actinic light. Baskerville and Riederer [27] state that ultraviolet light has very little effect upon the reaction but that intense illumination by light strong in the visible blue rays is much more effective. Philips [28] heated the chlorine-methane mixture and prevented explosions by packing the heated zone with sand, asbestos or bone black,[29] very similar to the method of smoothly chlorinating acetylene. At 300° to 400°, in the dark, the principal products are methyl chloride and carbon tetrachloride. Tolloczko

[24] Hilpert & Paunescu, *Ber.* *46,* 3479 (1913).

[25] Cf. U. S. Bur. Mines. Techn. Paper #255,-11, (1921). "Chlorination of Natural Gas" by Jones, Allison & Meighan.

[26] *J. Ind. & Eng. Chem.* *8,* 1090 (1916).

[27] *J. Ind. & Eng. Chem.* *5,* 5 (1913).

[28] *Am. Chem. J.* *16,* 361 (1894).

[29] Yoneyama & Ban [*J. Chem. Soc. Abs.* *1921,* I. 3] use bone black and fine calcium oxide at 250°.

and Kling[30] obtained a yield of 78 per cent carbon tetrachloride by chlorinating at 400° in contact with pumice, and impregnation of the pumice with cupric chloride is said to favor smooth chlorination. Chlorination at 400° is also described by Mackaye.[31] The effect of catalysts upon these reactions is of interest, particularly as regards increasing the yield of partially chlorinated products. Passing a mixture of the two gases through active charcoal at 90° was proposed by Mallet[32] in 1879 and Damoiseau[33] states that methyl chloride may be chlorinated mainly to chloroform by passing the proper gas mixture through animal charcoal heated to 250°–350°. Garner and Clayton[34] have recently patented a similar method, employing a specially activated charcoal as the catalyst. Recent experiments of Jones, Allison and Meighan[35] indicate that the carbons, particularly anthracite activated by steam at 700° F., are much more effective than silicious porous substances, such as pumice, asbestos, silica gels, porcelains and glass wool. Although the work of these investigators and others shows that chlorination occurs somewhat below 300° in the *absence* of catalysts, they employed temperatures within the range 375° to 400° in nearly all of their experiments with catalysts.

Ferric chloride and antimony pentachloride give poor results[36] but the work of the U. S. Bureau of Mines indicates that coke impregnated with iron or nickel gives the highest yields of chloroform, that activated carbons give the best yields of carbon tetrachloride and that coke impregnated with nickel, tin or lead gives slightly better yields of methyl chloride, using larger proportions of methane in the latter case. A total yield of about 90 per cent of chlorinated products, based upon the gas used, can be obtained.

Methyl chloride boils at — 23.7°; melts at — 103°; its critical temperature is 143°, critical pressure 66 atmospheres, critical density 0.37. The densities and vapor pressures are given in the following table.[37] The latent heat of evaporation at 0° C. is 176 B.T.U. per lb. or 98 kilogram-calories per kilogram, or 4.94 kilogram-calories per gram molecule.[37]

The reduction of carbon tetrachloride to chloroform by zinc and a

[30] *J. Soc. Chem. Ind. 32*, 742 (1913).
[31] U. S. Pat. 888,900.
[32] U. S. Pat. 220,397.
[33] *Compt. rend. 91*, 1071 (1880); *92, 42*, 145 (1881).
[34] U. S. Pat. 1,262,769.
[35] Loc. cit.
[36] Pfeifer, Mauthner & Reitlinger, *J. prakt. Chem.* (2), *99*, 239 (1919).
[37] Holst, *Refrigerating World, 1919*, May, p. 13.

DENSITY AND VAPOR PRESSURE OF METHYL CHLORIDE.

°C	*Density, referred to water at 30°F.*	*Pressure, absolute in atmospheres*
−50	.....	0.27
−40	1.024	0.47
−22	1.008	0.76
−11	1.000	1.00
− 4	0.991	1.16
− 0	0.987	1.27
+14	0.972	1.73
+32	0.995	2.49
40	0.945	2.91
50	0.936	3.51
60	0.925	4.20
68	0.915	4.83
90	0.892	6.91
100	0.883	7.96

little aqueous hydrochloric acid [38] and by finely divided iron in the presence of water [39] has been carried out and some such method appears to offer the best solution thus far proposed for the problem of manufacturing chloroform from methane.

The conversion of methane into hydrocyanic acid by passing a mixture of methane, hydrogen and nitrogen through an electric arc has been tried out on an industrial scale but details of the process have not been published.[40]

Rideal and Taylor have reviewed the hydrogenation of carbon monoxide to methane.[41] The industrial operation of the process would make illuminating gas much less toxic and increase its calorific value. The process might be of value in localities where natural methane is not available and where the methane could be utilized for a special purpose, for example, the manufacture of chlorinated methane products. Elworthy [42] proposed to remove the carbon dioxide from water gas, add hydrogen sufficient to form the mixture, $CO + 3H_2$, and effect the conversion to methane by passing over catalytic nickel at 250°. At one time Sabatier [43] attempted the industrial solution of the problem in a somewhat different manner. He noted that the carbon deposited from the conversion of CO to CO_2 and carbon at 500° in the presence of nickel, readily reacts with steam to form CO_2 and methane. By superposing the two reactions, passing water gas and superheated steam over the catalyst at 500°, mixtures consisting essentially of methane, hydrogen and carbon dioxide were produced. Reduced nickel at 250°–

[38] *Chem. Rev. 1896,* 88.
[39] A. W. Smith, U. S. Patent, 753,325 (1904).
[40] *Chem. Abs. 1914,* 1659.
[41] "Catalysis in Theory and Practice." 1919. p. 182.
[42] Brit. Pat. 12,461 (1902) ; 14,333 (1904).
[43] French Pat. 355,900 (1905).

300° in the presence of an excess of hydrogen has been found most effective,[44] but in practice considerable difficulty was experienced by poisoning of the catalyst by substances containing sulfur,[45] and the deposition of carbon on the catalyst and it was also found that at least five volumes of hydrogen are required for one volume of carbon monoxide. Carbon dioxide is reduced to methane in the presence of nickel quite rapidly at 350°.[46] The necessary excess of hydrogen can be obtained by the catalytic conversion of CO and steam to hydrogen and CO_2 and removing the latter, or by partially separating the carbon monoxide and hydrogen of water gas by liquefaction methods. Bedford finds that when the liquefaction process is carried out so that the uncondensed portion contains approximately 14 per cent carbon monoxide, the sulfurous impurities are removed with the liquefied CO and the resulting mixture has no appreciable poisoning effect on the catalyst. Bedford carried out the reaction in quartz tubes at 280°–300° and owing to the strongly exothermic character of the reaction, $CO + 3H_2 \longrightarrow CH_4 + H_2O + 48{,}900$ calories, the reaction maintains itself without external heating. In order to prevent the deposition of carbon the concentration of carbon monoxide was kept below 17 per cent, the resulting gas containing 28.3 to 31.8 per cent methane. By successive additions of carbon monoxide and repassage over the catalyst a gas mixture containing 76 per cent of methane can be obtained. Meredith [47] states that it is difficult to prevent the formation of nickel carbonyl in this process, although, as is well known, the decomposition of nickel carbonyl is rapid at temperatures as low as 200° C.

Ethane: The simple derivatives of ethane are quite familiar to all organic chemists and their reactions have been most frequently employed as type reactions in text books of organic chemistry. Yet ethane itself has never been a product of industrial interest, and the hydrocarbon has not been employed as the raw material for the manufacture of those derivatives which are so important. For example, ethylene, ethyl chloride and ethyl ether are all manufactured from ethyl alcohol. Changed economic conditions conceivably may change a great many of these processes. That ethane can be separated in quite a pure state from methane and propane, was first shown, in an analytical way, by Burrell, Seibert and Robertson,[48] who made use of the large differ-

[44] Jochum, *J. Gasbel, 57,* 73,103,124 (1914).
[45] Gautier, *Compt. rend, 150,* 1564 (1910).
[46] Sabatier & Senderens, *Compt. rend, 134,* 514, 689 (1902) ; Farbwerke M. L. & Br. *Brit. Pat.* 146,110 ; 146,114 (1920).
[47] Gas Age, *47,* 7 (1921).
[48] U. S. Bureau of Mines, Techn. Paper 104 (1915).

ences of the vapor pressures of these several hydrocarbons at low temperatures.

By the Linde or Claude methods of fractional distillations at low temperatures these gases may be easily separated; in fact, the separation of nitrogen and oxygen is considerably more difficult. Reference to the boiling-points of these several substances indicates this possibility.

	Boiling-Point, at 760 mm.	*Difference*
Nitrogen	—195.84°	12.85°
Oxygen	—182.99°	
Methane	—160. °	70.7°
Ethane [49]	— 89.3 °	
Propane [50]	— 44.1 °	45.2°

The following vapor pressure curves of liquid ethane were determined by Burrell and Robertson, Fig. I, and by Maas and McIntosh, Fig. II. Natural gas and possibly oil gas and petroleum still gases

ETHANE

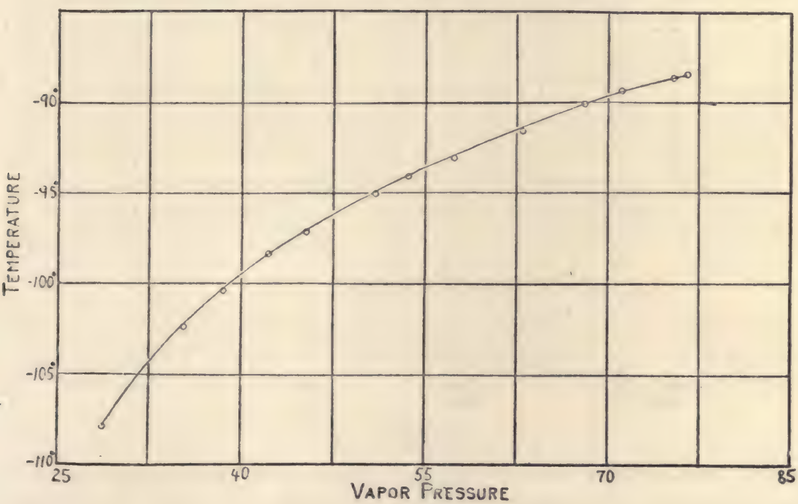


FIG. 2.

contain ethane in quantities sufficient for its separation on a large industrial scale; the high ethane content of many samples of natural gas, as determined by the old method of combustion and calculation, is undoubtedly inaccurate, as has been previously pointed out, but 10

[49] This value found by Burrell & Robertson, *J. Am. Chem. Soc.* 37, 1893 (1915); Maas & McIntosh give — 88.5° as the boiling-point of ethane, *J. Am. Chem. Soc.* 36, 737 (1914); Cardoso & Bell, *J. chim. phys.* 10, 497 (1913); found the value —84.1°; Maas & Wright, *J. Am. Chem. Soc.* 43, 1102 (1921) give the value — 88.3°.

[50] Burrell & Robertson, *J. Am. Chem. Soc*, 37, 2188 (1915).

to 12 per cent ethane is not uncommon. Practically pure ethane, separated in this manner, and cheap chlorine, present to organic chemists a great opportunity. The manufacture of ethyl chloride, ethylene, ethyl ether and ethyl alcohol from ethane is entirely feasible by methods now known but which are capable of great improvement.

The chemical properties of ethane are nearly identical with those of methane; it is less stable to heat and in contact with metallic nickel

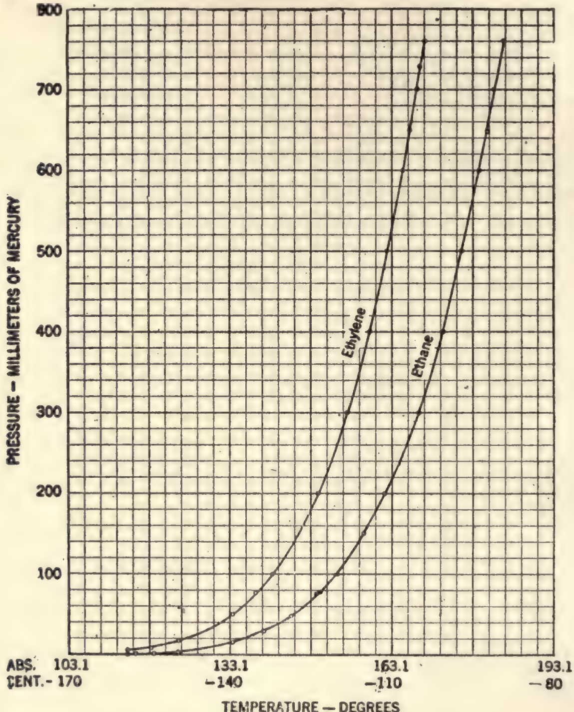


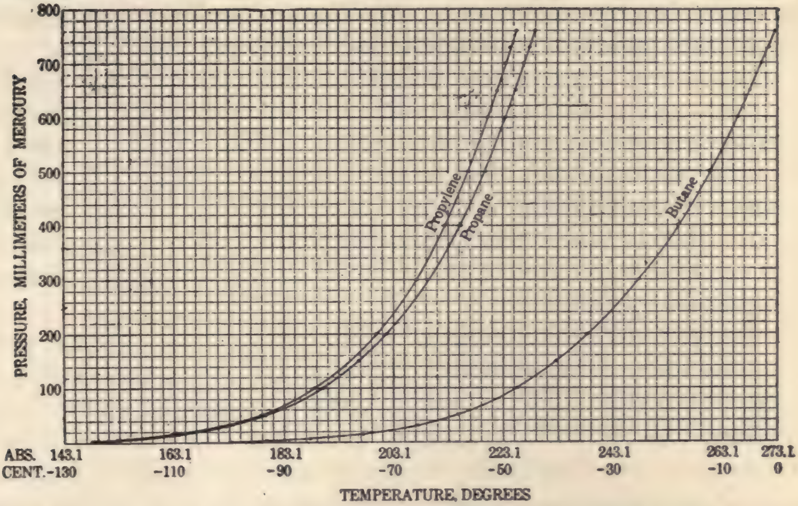
FIG. 1.

at 325° carbon is deposited and methane and hydrogen are formed.[51] It is absorbed by fuming sulfuric acid somewhat more rapidly than methane.[52] Slow oxidation below the temperature of actual ignition yields chiefly water, carbon dioxide, carbon monoxide and formaldehyde.[53] It is more readily chlorinated than methane and it is noteworthy, in the light of Michael's positive and negative theory of addition, that ethyl chloride on further direct chlorination yields chiefly ethylidene chlorine but in the presence of antimony pentachloride

[51] Sabatier & Senderens, *Compt. rend.* 124, 1360 (1897).
[52] Worstall, *J. Am. Chem. Soc.* 21, 249 (1899).
[53] Bone & Stockings, *J. Chem. Soc.* 85, 696 (1904).

ethylene chloride is the principal product.[54] No researches on the chlorination of ethane have recently been published.[55]

Propane: The principal raw materials utilized for the preparation of propane and its simple derivatives are acetone, glycerine, trimethylene glycol, propyl alcohol from fusel oil, and propylene from oil gas or petroleum still gases. Crude pyroligneous acid contains allyl alcohol, but no industrial use for it has been found. The hydrocarbon itself is not used as such or separated from natural gas or other gas mixtures containing it. Natural gas is the only source from which it



could be separated in quantity. For laboratory study it may conveniently be prepared by the catalytic decomposition of isopropyl alcohol, over alumina at 380°–400°, and the catalytic hydrogenation of the resulting propylene to propane.[56]

The vapor pressure curves of liquid propane, propylene and butane are shown in the accompanying figure.[57]

The chlorination of propane does not appear to have been studied since the work of Schorlemmer [58] in 1869, who noted the formation of n.propyl chloride (?), propylene chloride and more highly chlorinated products. Although the *monochlorides* of methane, ethane, pentane, and probably propane and butane can be converted into the corre-

[54] D'Ans. & Kautzsch, *J. prakt. chem.* (2), *80*, 310 (1909); V. Meyer & Müller, *Ber. 24*, 4247 (1891); Kronstein, *Ber. 54B*, I. (1921).
[55] Cf. Lacy, U. S. Pat. 1,242,208: chlorinates above 300°.
[56] Sabatier & Senderens, *Compt. rend. 134*, 1127 (1902).
[57] Burrell & Robertson, *J. Am. Chem. Soc. 37*, 2188 (1910).
[58] *Ann. 152*, 159 (1869).

sponding alcohols with good yields and ethylene chloride may be converted satisfactorily to the glycol, the more highly chlorinated derivative 1, 2, 3, trichloropropane behaves very differently. Caustic alkali yields β-epidichlorohydrine $CHCl = CH.CH_2Cl$ and α-derivative $CH_2 = CCl.CH_2Cl$, and alcoholic potash gives ethylchloroallyl ether, $C_2H_5O.C_3H_4Cl$. From what is known of the halogen derivatives of propane, it is very improbable that glycerine will ever be manufactured industrially by their means. Glycerine can be synthesized by adding HOCl to allyl chloride and hydrolysing the product, but when it is attempted to prepare allyl chloride by decomposing propylene chloride, the principal products are found to be α and β chloropropylene.

Butanes: Normal butane was made by Frankland in the attempt to isolate the hypothetical ethyl radical, by the reaction of ethyl iodide and metallic zinc. It has been prepared in a very pure state by Lebeau by treating n.butyl iodide with sodium amalgam in liquid ammonia.[59] Its boiling point at 755 mm. is 0.5°; critical temperature 151° to 152°. At 17° and 772 mm. pressure one volume of water dissolves 0.15 volumes; chloroform at 17° and 768 mm. dissolves 32.5 volumes of the gaseous hydrocarbon.

The most convenient source of n.butyl compounds is n.butyl alcohol from which a large number of simple derivatives may readily be prepared.[60] This alcohol is now a common commercial article, being obtained together with acetone by fermenting starch with a mould, *Amylomyces rouxii* studied by Fernbach and Strange, and by bacteria, probably *Bacillus granulobacter pectinovorum,* the latter process being developed by Weizmann.[61] The butyl alcohol produced in ordinary alcoholic fermentation and appearing in the fusel oil fore-runnings is isobutyl alcohol, $(CH_3)_2.CH.CH_2OH$.

The most convenient source of crude butane is the very light gasoline separated from natural gas or "casing head" gas. Garner and Cooper have described the isolation of crude butane from this source by the application of principles now well known in the industry.[62]

Butlerow [63] pointed out that two isomeric butanes were possible and synthesized isobutane by treating acetyl chloride with zinc methyl, according to the well-known Butlerow synthesis, forming the car-

[59] *Bull. Ac. Roy. Belg. 1908,* 300.
[60] Kamm & Marvel, *J. Am. Soc. 1920,* 299.
[61] Speakman, *J. Soc. Chem. Ind. 38,* 155 (1919); Weizmann, Brit. Pat. 4,845 (1915); Fernbach & Strange, Brit. Pat. 14,607 (1915); Fernbach, Brit. Patents, 109,969 (1917); 15,203, 15,204 and 16,925 (1911).
[62] U. S. Pat. 1, 307,353 (1919).
[63] *Ann. 144,* 1 (1867).

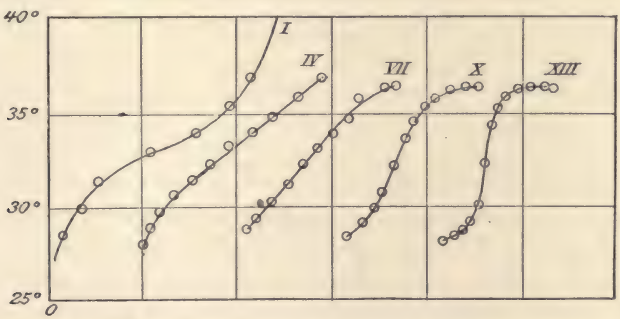
$$\textit{Isobutane:}\quad \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>CH-CH_3$$

binol $(CH_3)_3C.OH$. This was converted into the iodide which on reduction with zinc in the presence of water gave isobutane, an octane and isobutylene.

Isobutane boils at — 10.5° under 757 mm.; its critical temperature is 134° to 135°.[64]

The butanes are readily chlorinated by moist chlorine at ordinary temperatures.[65] Bromine reacts much less readily and on heating with bromine in a sealed tube, it is decomposed forming tetrabromethylene, $Br_2C = CBr_2$ as one of the products.[66] Isobutylene readily combines with hydrogen iodide to form tertiary butyl iodide.

The Pentanes: Both normal and isopentane occur in petroleum, at least in certain petroleums which have been carefully examined. The difficulty of separating these two hydrocarbons by fractional distillation is well shown by the work of Young,[67] whose results are expressed by the following figure:



Thirteen very careful fractional distillations and the use of a very efficient fractionating column were required to isolate these two hydrocarbons in fair degrees of purity.

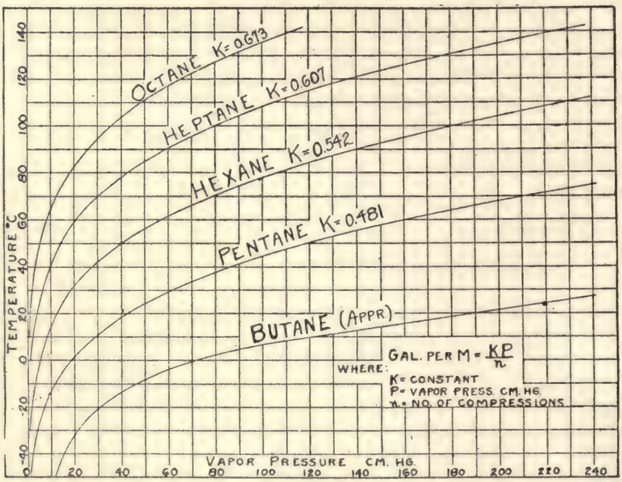
The vapor pressure curves of butane n.pentane, n.hexane, n.heptane and n.octane are given in the following table: [68]

The pentanes are chlorinated very much more readily than methane and ethane, i. e., at 0° in diffused daylight. The relative stability of

[64] Lebeau, loc. cit.
[65] Mabery & Hudson, *Am. Chem. J. 19*, 244 (1897).
[66] Weith, *Ber. 11*, 2244 (1878).
[67] *J. Chem. Soc. 73*, 906 (1898).
[68] Anderson, *J. Ind. Eng. Chem. 12*, 547 (1920).

the halogen derivatives of the series methane to pentanes inclusive has already been noted.

No satisfactory method of preparing these simple hydrocarbons seems to have been developed. The preparation of n.pentane by heating acetyl acetone with concentrated hydroiodic acid to 180° and by heating pyridine with the same reagent to 300° has been suggested. The action of amyl or iso-amyl bromides on magnesium, in ether, probably yields a little amylene and decanes,[69] but since n.pentane or isopentane can easily be separated from these by-products, the method



of decomposing amyl or iso-amyl-magnesium bromides by water would undoubtedly prove the most satisfactory method of preparing these hydrocarbons in a pure state. By the reduction of iso-amyl iodide by zinc fairly pure isopentane can be prepared,[70] and Ipatiev made isopentane by the hydrogenation of trimethyl ethylene.[71]

Tetramethylmethane, $C(CH_3)_4$, was prepared by reacting upon 2.2-dichloropropane with zinc methyl,

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>CCl_2 + Zn(CH_3)_2 \longrightarrow \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>C<\!\!\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} + ZnCl_2$$

This hydrocarbon[72] is remarkable for its relatively low boiling point, 9.5°, and relatively high freezing-point, —20°.

[69] Cf. Tschelinzeff, *J. Russ. Phys.-Chem. Soc.* *36*, 549 (1903) ; Tiffeneau, *Compt. rend.* *135*, 481 (1904).
[70] Frankland, *Ann.* *74*, 53 (1850) ; Just, *Ann.* *220*, 152 (1883).
[71] *Ber.* *42*, 2089 (1909).
[72] Lwow, *Z. f. Chem.* *1870*, 520.

Aschan[73] has studied the chlorination of the pentane and hexane fractions of petroleum and also the chlorination of isopentane, which hydrocarbon, Aschan claims, is present in all petroleums. The best yields of monochloropentanes are obtained by chlorinating with dry chlorine but moist chlorination leads chiefly to the formation of the two possible primary chlorides, small proportions of secondary chloride and no tertiary chloride. Dry chlorination yields all four possible monochlorides the properties of which are given by Aschan as follows:

	Boiling-Point	$D\frac{15}{15}$
4-chloro-2-methyl butane	99. –102.°	0.8692
3-chloro-2-methyl butane	90. – 93.°	0.8752
1-chloro-2-methyl butane	96. – 99.°	0.8818
2-chloro-2-methyl butane	85.5– 88.°	0.8692

The primary iso-amyl chloride made from natural fusel oil is converted almost quantitatively to the acetate and alcohol by heating with alcoholic potassium acetate at 200°. Isopentyl chloride is only very slowly acted upon by 2 per cent caustic potash at 60°–70°.

The Hexanes: Like the pentanes, normal hexane may readily be separated, in an impure state, from light petroleum distillates, and the preparation of pure n.hexane depends upon standard laboratory methods such as the reduction of secondary hexyl iodide (made from mannite) or the condensation of normal propyl iodide by metallic sodium.[74]

Like pentane it chlorinates readily and it also reacts rapidly with bromine in sunlight. The mixture of monochlorides contains about 10 per cent of the 1-chloro compound and about 45 per cent each of the 2 and 3 chloro derivatives.[75] Its reactivity to the halogens, to fuming sulfuric acid, to nitration by the dilute nitric acid method, and the properties of the simple derivatives, chlorides, alcohols, amines, carboxylic acid derivatives, etc., is almost identical with the chemical behavior of cyclohexane.

The Heptanes: Normal heptane enjoys the distinction of being the only saturated hydrocarbon, other than the solid paraffines formed by phytochemical processes. It is one of the major constituents in the volatile oil of the two American pines, *Pinus sabiniana* and *Pinus jeffreyi,* and also occurs in the "petroleum nuts," *Pittosporum resiniferum,* of the Philippines. How such a saturated hydrocarbon is formed in the living plant is entirely obscure; it is accompanied by

[73] *Chem. Abs. 14,* 3654 (1920).
[74] Michael, *Am. Chem. J. 25,* 421 (1901).
[75] Michael & Turner, *Ber. 39,* 2153 (1906).

no other substances, so far detected, which conceivably could have been the parent substance. Unsaturated hydrocarbons, the terpenes, are undoubtedly formed from alcohols, and it is well established that such decompositions occur in the leaves of plants. Pine needle oils commonly contain borneol and other alcohols although the oleoresins of these pines, when finally secreted in the resin ducts of the stem, contain only resin acids and unsaturated hydrocarbons. The fact that this particular hydrocarbon is one of an odd number of carbon atoms is also most unusual, since by far the great majority of the hydrocarbons, sugars and alcohols, fatty acids and ketones occurring in plants contain an *even* number of carbon atoms.

Normal heptane probably occurs in most light petroleum fractions, as in commercial gasoline.[76] Its separation from gasoline, however, in a reasonably pure state is a matter of the greatest difficulty. The raw material which has been employed for the preparation of the best known derivatives of n.heptane is oenanthol or n.heptyl aldehyde.[77] This aldehyde undergoes the usual aldehyde reactions, yields 1.1-dichloroheptane by treatment with PCl_5, and on reduction gives n.heptyl alcohol from which n.heptyl chloride can be made by the action of hydrogen chloride. This is the only one of the four possible monochlor derivatives of n.heptane which has been prepared in reasonable purity and identified as such. Only three of the possible 17 dichlorides are known, i. e., the 1-1, 4-4 and 1-7 derivatives. Until the discovery of the Grignard reaction which serves to build up any desired carbon structure up to 10 carbon atoms and with limitations, larger molecules, and also the discovery of catalytic hydrogenation by which means unsaturated hydrocarbons may be readily converted at low temperatures and in neutral reaction media, to saturated hydrocarbons, our knowledge of hydrocarbons of the paraffine series containing more than six carbon atoms was very limited indeed.

The physical properties of the known isomeric heptanes are as follows:

Name	*Structure*	*Boiling-Point*	*Density*
n.Heptane	$CH_3(CH_2)_5CH_3$	98.2–98.5°	0.7006– 0°
2-Methylhexane	$(CH_3)_2CH.(CH_2)_3.CH_3$	89.9–90.4°	0.7067– $\frac{0°}{4°}$
3-Methylhexane	$C_3H_7.CH(CH_3).C_2H_5$	90. –92. °	0.6865–$\frac{20°}{4°}$

[76] Young, *J. Chem. Soc.* 73, 906 (1898); Engler & Hofer, "Das Erdöl," Vol. I, 244 (1913).

[77] This aldehyde is readily prepared by the well known method of destructive distillation of castor oil, enanthol and undecylenic acid being formed.

Name	*Structure*	*Boiling-Point*	*Density*
3-Ethylpentane	$CH.(C_2H_5)_3$	95. –98. °	0.689 –27°
2, 2-Dimethylpentane	$(CH_3)_2C.C_3H_7$	78.°	0.6910 $\frac{0°}{0°}$
2, 4-Dimethylpentane	$(CH_3)_2CH.CH_2.CH.(CH_3)_2$	83. –84. °	0.7002 $\frac{0°}{0°}$
3, 3-Dimethylpentane	$(CH_3)_2C(C_2H_5)_2$	86. –87. °	0.7111 0°

The Octanes: Normal octane probably occurs in most light petroleum distillates, or gasolines. It is most readily prepared in a pure state by treating n.butyl iodide with sodium,[78] a reaction which is said to give better yields with alkyl halides of higher molecular weight than with the simpler ones. As typical examples of methods which may be employed in the synthesis of hydrocarbons, the methods employed in the preparation of the known octanes are given in reaction outline, as follows:

(1) *Normal octane.*[78]

$$2CH_3CH_2CH_2CH_2I + 2Na \longrightarrow NaI + CH_3(CH_2)_6.CH_3$$

(2) *2-Methylheptane.*[79]

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH.CH_2CHO + Mg\!<\!\begin{matrix} CH_2CH_2CH_3 \\ X \end{matrix} \longrightarrow$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH.CH_2\underset{\substack{|\\ OH}}{CH}.CH_2CH_2CH_3$$

$\longrightarrow$ corresponding iodide $\longrightarrow$ 2-methyl-heptane, by reduction with copperized zinc and hydrochloric acid.

(3) *3-Methylheptane.*[80]

$$CH_3CH_2CH_2I + CH_3CO\underset{\substack{|\\ Na}}{CH}.CO_2C_2H_5 \longrightarrow$$

$$CH_3CO\underset{\substack{|\\ CH_2CH_2CH_3}}{CH}.CO_2C_2H_5 \xrightarrow{10\%\ KOH} CH_3COCH_2CH_2CH_2CH_3 \longrightarrow$$

$$\longrightarrow CH_3\underset{\substack{|\\ C_2H_5}}{C}(OH).CH_2CH_2CH_2CH_3 \longrightarrow \text{corresponding iodide} \longrightarrow$$

3-methylheptane, by reduction as indicated above.

[78] Zincke, *Ann.* *152*, 15 (1869).
[79] L. Clarke, *J. Am. Chem. Soc.* *31*, 108 (1909).
[80] *Ibid.*, 558 (1909).

(4) *4-Methylheptane.*[81]

$$CH_3CH_2CH_2\underset{\substack{| \\ I}}{CH}.CH_3 + CH_3CO\underset{\substack{| \\ Na}}{CH}.CO_2C_2H_5 \longrightarrow$$

$$CH_3CO\underset{\substack{| \\ CH_3CH.CH_2CH_2CH_3}}{CH}.CO_2C_2H_5 \xrightarrow{10\%\ KOH} CH_3CH_2CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_2COCH_3$$

by reduction by sodium in moist ether $\longrightarrow$ alcohol $\longrightarrow$ iodide $\longrightarrow$ $CH_3CH_2CH_2 - \underset{\substack{| \\ CH_3}}{CH} - CH_2CH_2CH_3$

(5) *2.4-Dimethylhexane.*[82]

$$CH_3CO.CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_2CH_3 + Mg{<}\begin{matrix}CH_3 \\ I\end{matrix} \rightarrow$$

$$CH_3\underset{\substack{| \\ CH_3}}{C}(OH).CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_2CH_3$$

$\longrightarrow$ iodide, which by reduction $\longrightarrow$ $CH_3\underset{\substack{| \\ CH_3}}{CH}.CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_2CH_3$

(6) *2.5-Dimethylhexane. (Di-isobutyl)*

(a)[83] $2(CH_3)_2CH.CH_2I + 2Na \rightarrow (CH_3)_2CH.CH_2CH_2CH(CH_3)_2$

(b)[84] $$CH_3CO.\underset{\substack{| \\ CH_2CH{<}\begin{matrix}CH_3 \\ CH_3\end{matrix}}}{CH}.CO_2C_2H_5 \rightarrow CH_3CO.CH_2CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_3$$

by $Mg{<}\begin{matrix}CH_3 \\ I\end{matrix} \rightarrow CH_3\underset{\substack{| \\ CH_3}}{C}(OH).CH_2CH_2\underset{\substack{| \\ CH_3}}{CH}.CH_3 \rightarrow$ hydrocarbon as above

[81] L. Clarke, *Am. Chem. J. 39,* 87 (1908); *Ber. 40,* 352 (1907); cf. Clemmensen, *Chem. Abs. 6,* 2919 (1912).
[82] L. Clarke, *J. Am. Chem. Soc. 30,* 1144 (1908).
[83] Wurtz, *Ann. 96,* 365 (1855).
[84] L. Clarke, *J. Am. Chem. Soc. 31,* 586 (1909).

(7) *3.4-Dimethylhexane.*[85]

$$2CH_3CH_2COCH_3 \text{ (Methylethyl ketone)} \rightarrow 2CH_3CH_2CH(OH).CH_3$$

$$\rightarrow 2CH_3CH_2\underset{\underset{Br}{|}}{CH}.CH_3 + 2Na \rightarrow CH_3CH_2\underset{\underset{CH_3}{|}}{CH}.\underset{\underset{CH_3}{|}}{CH}.CH_2CH_3$$

(8) *2-Methyl, 3-ethylpentane.*[86]

$$\begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!>CH.COCH_3 + Mg\!<\!\begin{matrix}CH_3\\I\end{matrix} \rightarrow \begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!>CH.\underset{\underset{CH_3}{|}}{C}(OH).CH_3$$

$$\text{by methods given above} \rightarrow \begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!>CH.CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

(9) *2.2.3.3-Tetramethylbutane.*[87]

$$(CH_3)_3C.Br + (CH_3)_3C.MgBr \longrightarrow MgBr_2 + (CH_3)_3C-C(CH_3)_3$$

Eighteen isomeric octanes are theoretically possible.

The physical properties of the known octanes are as follows:

Name	Structure	Boiling-Point	Density
n.Octane	$CH_3(CH_2)_6CH_3$	125.8°	$0.7185\frac{0^\circ}{4^\circ}$
2-Methylheptane	$(CH_3)_2CH.(CH_2)_4CH_3$	116. °	$0.7035\frac{15^\circ}{15^\circ}$
3-Methylheptane	$CH_3CH_2\underset{\underset{CH_3}{\mid}}{CH}.(CH_2)_3CH_3$	117.6°	$0.7167\frac{15^\circ}{15^\circ}$
4-Methylheptane	$C_3H_7.\underset{\underset{CH_3}{\mid}}{C}.C_3H_7$	118. °	$0.7217\frac{15^\circ}{}$
2.4-Dimethylhexane	$C_2H_5\underset{\underset{CH_3}{\mid}}{CH}.CH_2\underset{\underset{CH_3}{\mid}}{CH}CH_3$	109.8°–110. °	$0.7083\frac{15^\circ}{15^\circ}$
2.5-Dimethylhexane	$(CH_3)_2CH.CH_2CH_2CH(CH_3)_2$	108.3°–108.5°	$0.6993\frac{15^\circ}{15^\circ}$
3.4-Dimethylhexane	$C_2H_5.\underset{\underset{CH_3}{\mid}}{CH}.\underset{\underset{CH_3}{\mid}}{CH}.C_2H_5$	116. °–116.2°	$0.7165\frac{25^\circ}{4^\circ}$
2-Methyl, 3-ethylpentane	$CH_3\underset{\underset{CH_3}{\mid}}{CH}.\underset{\underset{C_2H_5}{\mid}}{CH}.CH_2CH_3$	114. °	$0.7084\frac{15^\circ}{}$
2.2.3.3.-tetramethylbutane	$(CH_3)_3C.C(CH_3)_3$	106. °–107. °	*

*Remarkable for its high melting-point. 103°-104°.

[85] Norris & Green, *Am. Chem. J.* *26*, 313 (1901).
[86] L. Clarke, *Am. Chem. J.* *39*, 572 (1908).
[87] Henry, *Compt. rend.* *142*, 1075 (1906).

The Nonanes and Decanes: Pure normal nonane boils at 149.5° and n.decane at 173°. The petroleum fraction boiling chiefly at 150°–170°, therefore, consists chiefly of these two hydrocarbons, when derived from petroleums of the Pennsylvania type.[88] This particular fraction is a regular commercial article, being sold as a turpentine substitute. Its volatility or rate of evaporation and solvent power for oils and resins is practically identical with that of turpentine.[89]

2.6-Dimethyl Octane,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH.(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2CH_3$$

is of interest in that it possesses the carbon structure of the aliphatic so-called terpenes, myrcene and ocimene, $C_{10}H_{16}$, and also the alcohols geraniol, linalool and citronellol and their corresponding aldehydes. Many of the terpenes proper and their alcohols are very probably related genetically to these alcohols and aldehydes and it is therefore a matter of theoretical interest, what substance or substances in living plants yield alcohols or hydrocarbons of the carbon structure of 2.6-dimethyl octane. This saturated hydrocarbon has not been found in nature but is readily made by hydrogenation of myrcene or ocimene, or the alcohols geraniol or linalool.[90]

Paraffines $C_{10}H_{22}$ *to* $C_{60}H_{122}$. Of the hydrocarbons of this series all the normal paraffines up to $C_{26}H_{54}$ are known, and also a few hydrocarbons higher in the series have been definitely characterized. Most of what is known of the synthesis of the solid paraffines is found in three papers published by Krafft,[91] who employed the following methods in their preparation:

(1) Heating fatty acids with hydriodic acid and phosphorus, in sealed tubes, to 240°.
(2) Condensation of n.alkyl primary iodides by means of sodium.
(3) Preparation of ketones by heating the calcium salts of fatty acids; conversion of the ketones, to dichlorides by PCl_5 and reduction by HI and phosphorus,

$$C_{17}H_{35}CO.C_6H_{13} \rightarrow \text{dichloride} \rightarrow \text{hydrocarbon}$$

[88] Mabery, *Am. Chem. J. 19*, 419, 482 (1897).

[89] Much of the special naphtha sold for thinning paint and varnish boils chiefly over the range 160°-190° or considerably above the boiling-point range of turpentine. Oils used in paints and varnishes are miscible in both petroleum naphtha and turpentine but copals are sparingly soluble in both solvents. Fusion of copals, as in varnish making, partially decomposes them and the longer the fusion, or the greater the decomposition, the more oil and thinner can be incorporated in the varnish without partial precipitation of resins.

Old oxidized turpentine leaves a resinous film on evaporation and the presence of organic peroxides in such turpentine accelerates the oxidation or "drying" of linseed oil. However, the difference in behavior on drying films of paint or varnish thinned with freshly distilled turpentine, or with petroleum naphtha, is not appreciable.

[90] Willstätter, *Ber. 41*, 1478 (1908); Enklaar, *Ber. 41*, 2084 (1908).

[91] *Ber. 15*, 1697 (1882); *19*, 2223 (1886); *29*, 1323 (1896).

Peterson[92] employed the method of electrolysing the fatty acid soaps and Mai[93] heated the barium soaps with sodium methoxide. Formates at 290°–300°[94] decompose to paraffines.

Crystalline paraffines have been noted from a wide variety of sources but commercial paraffine is derived principally from certain petroleums and to a lesser extent from shale oil, ozokerite, and the distillates obtained by the carbonization of coal or lignite at low temperatures. The constitution of the paraffines made by synthesis according to the methods indicated above, may reasonably be inferred from the methods employed in their preparation, but as regards the crystalline paraffines found in the various pyrolytic distillates and in natural waxes and essential oils we know practically nothing more than may be inferred from their melting-points, and these values may be very misleading. Thus Krafft[95] prepared a series of paraffines, by fractional crystallization, from the crude paraffine isolated from an oily distillate from lignite. On the basis of their melting points, varying from 22.5° to 76°, the various crystal fractions are described as eighteen distinct substances but many of the specimens so prepared were probably mixtures. It is probable that many of these crystalline paraffines are not normal hydrocarbons, for example, n-eicosane, $C_{20}H_{42}$, melts at 36.7° (made by condensing n.decyl iodide by sodium) but an isomeric hydrocarbon melting at 69° has been reported from four different natural sources.

It is of interest to note the number of essential oils and other natural products which contain solid paraffines, and that most of them evidently bear no relation to the natural fatty acids, having many more carbon atoms than these acids.

Source	Melting-Point
Kaempferia galanga (about 50% of the essential oil)[96]	10.°
Rose oil	22.°
Jaborandi leaves	28°–29.°
Rose oil	40°–41.°
Birch buds	50.°
Camomile oil	53°–54.°
Orange blossoms	55.°
Eucalyptus oils[97]	55°–56.°
Sassafras leaves	58.°
Bees-wax; Virginia and Kentucky tobacco[98]	59.5°

[92] *Z. f. Electroch.* *12,* 144 (1906).
[93] *Ber.* *22,* 2134 (1889).
[94] Fr. Bayer & Co. *J. Chem. Soc. Abs.* *1918,* I, 209.
[95] *Ber.* *40,* 4779 (1907).
[96] Schimmel & Co. *Semi-Ann. Rep.* *1903,* I, 43.
[97] Smith, *Chem. Abs.* 8, 399 (1914); in Eucalyptus acervula, E. paludosa and E. smithii.
[98] Thorpe & Holmes, *J. Chem. Soc.* *79,* 982 (1901).

Source	Melting-Point
Verbena	62.5°
Arnica, essential oil; pelargonium	63.°
Camomile, Roman	63°–64.°
Dill oil; Cistus, several species; Chrysanthemum cineraraefolium...	64.°
Wintergreen oil, from Betula and Gaultheria	65.5°
Bees-wax; leaves of European olive; Kentucky and Virginia tobacco; seeds of Brucea sumatrana; Lippia scaberrina; Micromeria chamissonis; Grindelia robusta; Gymnene sylvestre	68.1°
Eriodictyon californicum; leaves of European olive; Arthusa cynapium	74.7°
Evodia simplex	80°–81.°

Paraffines are also found in the mineral *ozokerite,* which is mined near Boryslaw, Galicia, and in Wasatch and Utah counties, Utah. Refining of ozokerite by concentrated sulfuric acid yields *ceresine,* which is valued for its relatively high melting point. When ozokerite is distilled crystalline paraffine, about 40 per cent, can be separated from the distillate, and the undistilled residue is ozokerite pitch or "okonite." Fractional crystallization of the solid waxes in Galician ozokerite gives a series of fractions the lowest melting at about 54° and the highest melting at 92.8°–93.2°.[99] Practically nothing is known of the nature of these hydrocarbons in refined ceresine beyond the fact that their analyses indicate the composition C_nH_{2m+2} and that their chemical behavior is like that of other solid paraffines.

The crystallization of paraffine is considerably affected by the viscosity of the oil from which it is crystallized and also the presence of asphaltic matter seriously interferes with the crystal growth. With increasing viscosity of the oil solvent the crystal size diminishes.[100] The exact nature of the so-called "amorphous wax" is not known but repeated distillation of oils containing much paraffine yields cleaner distillates from which large crystals are obtainable without difficulty. According to Rakuzin [101] crude petroleums contain crystallizable paraffine although its crystallization is greatly interfered with by asphaltic substances present. He is therefore opposed to Zaloziecki's views as to the presence of "protoparaffine" in crude petroleums, but there is no doubt that complex substances such as the "kerogen" of oil shale, peat and lignite, yield paraffine only when decomposed, as by heat.

Paraffine is remarkably insoluble in most organic solvents. The solubility of a paraffine fraction, melting-point 64° to 65° from Galician ozokerite, in petroleum ether is as follows: [102]

[99] Engler, "Das Erdoel," Vol. I, 667.
[100] Cf. Fuchs, *Petroleum 14,* 1281 (1919).
[101] *J. Russ. Phys.-Chem. Soc. 1913,* 1544; *J. Chem. Soc. Abs. 1914,* I, 489.
[102] Pawlewski, *Ber, 21,* 2973 (1888).

Solvent	g. paraffine in 100 g. solvent
Carbon bisulfide	12.99
Petroleum ether, boiling-point below 75°	11.73
Acetic acid, glacial	0.06

Since petroleum ether and glacial acetic acid are miscible in all proportions, these two solvents are recommended for recrystallizing paraffine. In industrial practice the oil and low-melting wax is permitted to drain slowly from the crude crystals in warm chambers, i. e., the "sweating process."

By several fractional distillations, at 40 mm., Mabery [103] separated commercial paraffine into several fractions, the lowest melting at 48° and the highest at 62°–63°.

The dielectric constant of paraffine is such that large quantities are used for the purpose of electrical insulation, usually in cases where the material is not subjected to temperatures high enough to melt the wax. Comparisons of the dielectric constant of paraffine and other common insulating materials, are as follows: [104]

	E
Paraffine, crude brown	2.07
" melting-point 44°-46°	2.105
" " " 54°-56°	2.145
" double refined	1.94
Asphalt	2.68
Amber	2.80
Shellac	3.10
Gutta-percha	4.43
Bees-wax	4.75

The specific heat of paraffine wax is a linear function of the temperature; at 100° it is 0.6307, at 0° = 0.47, at — 100° = 0.325 and at — 180° = 0.199.[105] The latent heat of fusion of commercial paraffine wax, calculated from the lowering of the freezing point on adding substances of known molecular weight, ranges from 38.9 to 43.9 calories.[106]

Paraffine wax is generally considered to be a very inert material but it is attacked by nitric acid and by sulfuric acid at slightly elevated temperatures, oxidation rather than nitration or sulfonation being the principal result. It reacts readily with sulfur on heating to about 200°, evolving hydrogen sulfide; in fact, this reaction serves as an admirable method for the laboratory preparation of hydrogen sulfide, particularly where the gas is not continually needed and the apparatus must stand

[103] Cf. *Am. Chem. J.* *33*, 251 (1905).
[104] Landolt-Börnstein, *"Physikalisch-Chemische Tabellen," 1912*, pp. 1212.
[105] Nernst, *J. Chem. Soc. Abs.* *108*, II, 263 (1910); Bushong & Knight, *J. Ind. & Eng. Chem.* *12*, 1197 (1920).
[106] Kozicki & Pilat, *J. Soc. Chem. Ind.* *37*, 681 A (1918).

PHYSICAL PROPERTIES OF THE SIMPLER PARAFFINES.
(Methane to Pentanes, inclusive.)

Name	*Structure*	*Boiling-Point* °C	*P mm.Hg*	*Melting-Point* °C	*Crit. Temp.* °C	*Crit. Pressure Atm.*	*Latent Heat of Evaporation*	*Density*		*Reference*
Methane	CH_4	−164.	760	−184.	−82.	55.	130 cal. per g.	1 liter at 0°C 760mm. 0.7168g; d 0.415 at −164°		110, 111, 112, 113
Ethane	C_2H_6	−84.1	749	−172.1	34.	50.2	260 cal. per g.	1 liter, 0°C 760mm. 1.3562		114, 111, 113; 115; 116
Propane	C_3H_8	−45.	760	....	97.	44.	....	0.536	0°	115. 116, 117
n.Butane	$CH_3CH_2CH_2CH_3$	+0.5	755	....	151.	....	....	0.60	0°	118
Isobutane	$\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_3$	−10.5	757	....	134.5	....	....	....	..	118
n.Pentane	$CH_3(CH_2)_3CH_3$	+36.3	760	−147.5	197.2	33.26	74.89	0.6337	15°	119, 120, 121
								0.6475	0°	122
								0.6453	$\frac{0°}{4°}$	123
Isopentane	$\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2CH_3$	27.94	760	....	187.8	32.97	6397 (mol. ht.)	0.6394	$\frac{0°}{4°}$	123
2, 2-Dimethylpropane	$C(CH_3)_4$	9.5		−20.		....		0.6251	14.4	125; 124, 123

[110] Moissan & Chavanne, *Compt. rend.* *140*, 409 (1905).
[111] Baume & Perrot, *Compt. rend.* *148*, 39 (1909).
[112] Hunter, *Chem Zentr.* *1906*, II, 485 : Boiling-point-Pressure curve.
[113] Satterly & Patterson, *Tr. Roy. Soc. Canada*, *13*, 123 (1919) : latent heat.
[114] Ladenburg & Krügel, *Ber.* *33*, 638 (1900).
[115] Olszewski, *Ber.* *27*, 3306 (1894) ; boiling-point critical values.
[116] Hainlen, *Ann.* *282*, 245 (1894) ; boiling-point.
[117] Lebeau, *Compt. rend.* *140*, 1455 (1905) ; critical values, boiling-point.
[118] Lebeau, *J. Chem. Soc. Abs.* *1908*, I, 749. boiling-point, critical temperature.
[119] Young, *J. Chem. Soc* *71*, 446 (1897) : boiling-point.
[120] Guttman, *J. Am. Chem. Soc.* *29*, 347 (1907) : melting-point.
[121] Perkin, *J. prakt. chem.* (2) *31*, 488 (1885) : density.
[122] Jahn, *Z. physik. Chem.* *11*, 790 (1894) : latent heat.
[123] Young *Trans. Roy. Soc. Dubl.* *12*, 374 (1910) : critical values, density.
[124] Timmermans, *Bull. Soc. Roy. Belg.* *24*, 244 (1910) : boiling-point.
[125] Lwow, *Z. f. chem.* *1870*, 520 : melting-point, boiling-point.

Name	Structure	Melting-Point °C	Boiling-Point °C	Pmm.Hg	Density	Reference
n.Hexane	$CH_3(CH_2)_4CH_3$	—93.5°	68.95	760	0.67703 $\frac{0°}{4°}$	126
Isohexane	$\frac{CH_3}{CH_3} > CH(CH_2)_2CH_3$		60.5°	760	0.6583 $\frac{17°}{4°}$	127
			61.		0.6765 $\frac{0°}{0°}$	
n.Heptane	$CH_3(CH_2)_5CH_3$	—94.75°	98.43°	762	0.70048 0°	128, 129
					0.6815 $\frac{20°}{0°}$	
n.Octane	$CH_3(CH_2)_6CH_3$	—98.2°	125.8°	760	0.7185 $\frac{0°}{4°}$	120, 130
					0.7019 20.6°	131, 133
n.Nonane	C_9H_{20}	—51.°	149.5°	760	0.733 0°	132
n.Decane	$C_{10}H_{22}$	—32.°	172.°	760	0.7454 0°	132, 133
			63.°	15	0.7304 20°	
n.Undecane	$C_{11}H_{24}$	—26.5°	194.5°	760	0.7559 $\frac{0°}{4°}$	
			81.°	15	0.7411 $\frac{20°}{4}$	132
n.Dodecane.	$C_{12}H_{26}$	—12.°	214.5°	760	0.7655 $\frac{0°}{4°}$	
			98.°	15	0.7511 $\frac{20°}{4°}$	132
n.Tridecane	$C_{13}H_{28}$	—6.2°	234.°	(760)	0.7571 $\frac{20°}{4°}$	
			114.°	(15)		132

[126] Young, *J. Chem. Soc. 73,* 906, 930 (1898) ; boiling-point.
[127] Zelinsky, *Ber. 40,* 4743 (1907) : boiling-point, density.
[128] Kishner, *Chem. Zentr. 1900,* I, 957 : density : de Forcrand, *Compt. rend. 172,* 31 (1921).
[129] Young, *J. Chem. Soc. 73,* 675 (1898) : boiling-point, density.
[130] Young, *J. Chem. Soc. 77,* 1145 (1900) ; *83,* 56 (1903) : boiling-point, density.
[131] Eijkman, *Chem. Zentr. 1907,* II, 1209 : density.
[132] Krafft, *Ber. 15,* 1692 (1882).
[133] Louguinine, *Compt. rend. 121,* 556 (1895) : latent heat.

PHYSICAL PROPERTIES OF THE SIMPLER PARAFFINES (*Cont.*).

Name	*Formula*	*Melting-Point*	*Boiling-Point* °C	P mm.Hg	*Density*	*Reference*
n.Tetradecane	$C_{14}H_{30}$	+ 5.5°	252.5°	(760)	$0.7645\ \frac{20°}{4°}$	134
			129.5°	(15)		
n.Pentadecane	$C_{15}H_{32}$	10.°	270.5°	(760)	$0.7689\ \frac{20°}{4°}$	135
			144.°	(15)		
n.Hexadecane	$C_{16}H_{34}$	19. –20.°	287.5°	(760)	$0.7707\ \frac{25°}{4°}$	132
			157.°	(15)		
n.Heptadecane	$C_{17}H_{36}$	22.5°	303.°	(760)	$0.7766\ \frac{22.5°}{4°}$	135
			170.°	(15)		
n.Octadecane	$C_{18}H_{38}$	28.°	317.°	(760)	$0.7768\ \frac{28°}{4°}$	134
			181.5°	(15)		
n.Nonadecane	$C_{19}H_{40}$	32.°	330.°	(760)	$0.7774\ \frac{32°}{4°}$	137
			193.°	(15)		138
n.Eicosane	$C_{20}H_{42}$	36.7°	205.°	(15)	$0.7779\ \frac{36.7°}{4°}$	137
n.Heneicosane	$C_{21}H_{44}$	40.4°	215.°	(15)	$0.7783\ \frac{40.4°}{4°}$	137
n.Docosane	$C_{22}H_{46}$	44.4°	224.5°	(15)	$0.7782\ \frac{44.0°}{4°}$	137
n.Tricosane	$C_{23}H_{48}$	47.7°	234.°	(15)	$0.7785\ \frac{47.7°}{4°}$	137
n.Tetracosane	$C_{24}H_{50}$	51.1°	243.°	(15)	$0.7786\ \frac{51.1°}{4°}$	132

[134] Krafft, *Ber.* *19*, 2223 (1886).
[135] Mai, *Ber.* *22*, 2134 (1889).
[136] Oddo, *Gazz. Chim Ital.* *31*, I. 347 (1901).
[137] Krafft & Weilandt. *Ber.* *29*, 1323 (1896)
[138] Schaal, *Ber.* *40*, 4787 (1907).

Name	Formula	Melting-Point	Boiling-Point	Density	Reference
n. Pentacosane	$C_{25}H_{52}$	53.8–54.°	282.° (40)	0.7911 $\frac{60°}{4°}$	139
n. Hexacosane	$C_{26}H_{54}$	56.8–57.°	....	....	140
n. Heptacosane	$C_{27}H_{56}$	59.5°	270.° (15)	0.7796 $\frac{59.5°}{4°}$	137
n. Octacosane	$C_{28}H_{58}$	60.°	316.–318.° (40)	....	141
n. Nonacosane(?)	$C_{29}H_{60}$	63.6–64.1°	....	....	140
n. Triacontane	$C_{30}H_{62}$	66.1°	....	....	142
n. Hentriacontane	$C_{31}H_{64}$	68.1°	302.° (15)	0.7808 $\frac{68.1°}{4°}$	137
n. Dotriacontane	$C_{32}H_{66}$	70.5°	310.° (15)	0.7754 $\frac{70.5°}{4°}$	134
n. Tritriacontane(?)	$C_{33}H_{68}$	71.8°	....	....	140
n. Tetratriacontane.	$C_{34}H_{70}$	72.9°	....	....	140
n. Pentatriacontane	$C_{35}H_{72}$	74.7°	331.° (15)	....	132
n. Hexatriacontane(?)	$C_{36}H_{74}$	76.°	....	....	140
....	$C_{60}H_{122}$	101. –102.°	....	....	143

[139] Mabery, *Am. Chem. J.* *33*, 288 (1905).
[140] Krafft, *Ber.* *40*, 4783 (1907).
[141] Mabery, *Am. Chem. J.* *28*, 195 (1902).
[142] Peterson, *Z. Elektrochem.* *12*, 144 (1906).
[143] Struve, *Ann.* *362*, 123 (1908).

idle for long periods.[107] Chlorine reacts rapidly when passed into the melted wax at about 125°, or in solution in carbon tetrachloride. Such a chlorinated product, containing about 33 per cent chlorine, has been employed as a solvent for chloramine-T, about 10 per cent of this germicidal substance dissolving in the "chlorocosane" at ordinary temperatures.[108] The oxidation of paraffine by air or oxygen at 120°–160° has already been referred to (see p. 52). Paraffine is also less stable to heat than is sometimes believed. Distillation, at ordinary pressure, of a wax melting at 52° causes a decrease in melting-point due to decomposition of about 4°. In the old fashioned cracking process as carried out to increase the yield of kerosene, the wax often crystallizes from the distillate in fine large crystals, due largely to decrease in the viscosity of the distillate, but, according to Mabery,[109] paraffine is actually decomposed during the process.

Notes on the Refining of Petroleum Distillates.

Petroleum distillates are refined with the object of removing offensive odors, removing or lightening the color and also rendering the oils more stable in the sense that certain constituents which oxidize readily with darkening of color and formation of acids or resinous substances are removed. The physical properties of the various fractions are but very slightly changed by refining, unless the lowering of the congealing point, or cold test, by the removal of paraffine wax may be considered as a refining operation. When first distilled from the crude oils the lighter fractions, including gasoline and kerosene, are nearly free from color and the lubricating oil fractions are clear shades of amber, brown or reddish brown, but on standing in contact with air, unrefined gasoline and kerosene become yellow and the lubricating distillates become very dark in color. These color changes do not take place appreciably in well refined oils.

Offensive *odors* are generally pronounced in the case of the more volatile oils, gasoline and kerosene, particularly when these are made from heavier oils by pyrolytic processes. The offensive odor of these distillates is commonly attributed to olefines but, with the exception of conjugated di-olefines such as cyclohexadiene and cyclopentadiene present in light oil gas condensates, the odors of pure unsaturated hydrocarbons are mild and not offensive. The conjugated di-olefines

[107] Fuel oil or lubricating oil also gives H_2S on heating with sulfur.
[108] Dakin & Dunham. *Chem. Abs.* *12*, 1079 (1918).
[109] *Proc. Am. Phil Soc.* *1897*, 135.

have a sharp irritating odor suggestive of allyl alcohol or acrolein, but less pronounced. Unsaturated hydrocarbons generally develop objectionable odors on long standing due to oxidation, for example turpentine when fresh is very sweet and pleasant in odor, deteriorates by air oxidation, formic acid being one of the products formed. The constituents which are chiefly responsible for the objectionable odors of petroleum distillates are derivatives containing sulfur, nitrogen bases and naphthenic acids. These are very efficiently removed by the usual processes of refining with concentrated sulfuric acid and washing with caustic alkali, although special methods have to be resorted to in order to remove sulfur derivatives from oils derived from certain crudes, for example the Frasch copper oxide method as applied to petroleum of the Lima-Indiana field. *Nitrogen bases* in the more volatile distillates possess odors closely resembling pyridine. These simpler nitrogen bases are generally absent in the case of gasoline and kerosene distilled directly from crude petroleums, but are present in pyrolytic gasolines, unless made from nitrogen free oil. Petroleums of the Mid-continent, Gulf coast, California and Mexican fields on distilling under pressure yield volatile malodorous nitrogen bases. Mabery has investigated the nitrogen bases present in California petroleum and concludes that they are quinoline derivatives. When light distillates, e. g., motor fuel or kerosene, containing the simpler nitrogen bases, are treated with copper oxide, as by the Frasch method, the oxide combines with the organic bases and treatment of the resulting copper oxide compound with caustic alkali liberates the nitrogen bases. In ordinary practice, however, the organic bases are very efficiently removed by treating with concentrated sulfuric acid. When the acid sludge is diluted with water to precipitate oil and tarry matter, salts of the organic bases and a large proportion of the alkyl sulfuric esters, derived from the unsaturated hydrocarbons, remain in solution in the diluted acid. When this diluted acid is concentrated by the usual process of open pan heating and evaporation, this dissolved organic matter carbonizes and causes the destruction of a portion of the acid. The charring of this organic matter with the separation of carbon seriously interferes with the operation of cascade evaporating systems by clogging of the overflow lips.

The tarry matter precipitated by diluting the sludge derived from treating lubricating oils, also generally contains nitrogen bases, as can readily be shown by heating or distilling with an excess of lime, but the quantity of ammonia thus obtainable is too small to be of industrial interest.

Sulfuric acid is also very effective in removing *naphthenic acids*, as was first shown by Zaloziecki,[144] and Gurwitsch [145] later showed that this removal of naphthenic acids is not merely a solution effect and that far greater proportions of the naphthenic acids present pass into the acid layer than corresponds to the proportions required by the law of partition coefficients. These observations are in accord with the findings of Kendall and Carpenter who showed that a very wide variety of organic substances containing oxygen, e. g., aliphatic and aromatic acids, ketones, aldehydes, and phenols, form addition products with concentrated sulfuric acid and they regard these addition products as oxonium compounds. American petroleums do not contain conspicuous proportions of naphthenic acids, as do most of the Russian oils, but many of the Gulf Coast oils contain naphthenic acids of high boiling-point. These high boiling naphthenic acids are removed from the lubricating oil distillates by alkali. They are nearly odorless and their alkali soaps are very easily salted out of solution on account of their large molecular weight. They have apparently not been investigated and nothing definite regarding their empirical composition or chemical character is known. They are not recovered in present refinery practice.

Practically nothing is known of the nature of the *coloring matters* in petroleum distillates. When such oils darken by air oxidation, amorphous asphalt-like substances are formed. Sulfuric acid is very effective in removing coloring matter, which is readily understood if the coloring matter consists largely of substances containing oxygen or nitrogen. It is improbable that these coloring matters are hydrocarbons, since the few colored hydrocarbons which are known contain conjugated unsaturated groups, as in the hydrocarbons of the fulvene series. Some writers regard the removal of such coloring matter by sulfuric acid as a purely physical or colloid phenomenon.[146] However, as all refiners know, it is necessary to use concentrated sulfuric acid in order to hold the tarry matter in solution, since in addition to the small amount of coloring matter present in the original unrefined lubricating oil, constituents are present which yield tar on treating with acid. Although water white gasoline and kerosene can be made without great difficulty, it is impossible entirely to remove the color from lubricating oils by sulfuric acid (or oleum) and alkali treatments.

[144] *Chem. Ztg. 1892,* 905.
[145] *Z. f. physik. Chem.* 87, 323 (1914).
[146] Ubbelohde, *Petroleum, 4,* 1395; Schulz, *Petroleum,* 5, No. 4 and 8.

Pale yellow viscous oils can be made in this way which are practically tasteless (liquid paraffine oil) but filtration through fuller's[147] earth, bone black or similar material, or distillation in vacuo, must be resorted to in order to obtain colorless oil such as is desired for pharmaceutical purposes.

The *fluorescence* of petroleum distillates is due to substances which are largely removed by sulfuric acid, although several treatments with concentrated acid followed by treatments with oleum (15% SO_3) are necessary entirely to remove them. This property also has been regarded by some writers as being due to particles of sulfur, carbon or other substance in a colloidal degree of dispersion, or due to the presence of substances having extremely large molecules. Although such mixtures are not optically homogenous and do show pronounced Tyndall effects, true fluorescence is not observed in aqueous or oil suspensions. Most petroleum distillates and certain crude petroleums which are sufficiently free from asphaltic matter, such as light Pennsylvania crudes, exhibit green, bronze-green, bluish green or clear blue fluorescence. Examination of carefully filtered fluorescent oils in a quartz ultramicroscope of the Zsigmondy type shows no particles in suspension.[148] When sulfuric acid sludge is diluted with water and filtered to remove oil and tar the resulting aqueous solutions are usually highly fluorescent. In other words, the fluorescent substances have been sulfonated to water soluble sulfonic acids. It is probable, therefore, that the extremely small quantities of fluorescent substances which are present in petroleum are highly condensed or benzenoid hydrocarbons.[149] Such fluorescent substances are commonly formed when any organic substance is charred, for example, boiled linseed oil exhibits fluorescence if even slight carbonization occurs during the boiling process. The heavy waxy distillates obtained toward the end of the heating of an old-fashioned coking still are highly fluorescent.

For various trade reasons it is sometimes desirable to modify the fluorescence and so-called "de-blooming" reagents are sometimes added to the oil. Thus nitronaphthalene is sometimes employed for this purpose. It is well known that the fluorescence of all organic substances which possess this property is greatly modified by various solvents

[147] It is probable that the color absorbing qualities of fuller's earth are dependent upon the presence of partially dehydrated amorphous silica. Certain American refineries have recently manufactured a bleaching material superior to fuller's earth, by treating natural talc-like hydrated silicates with sulfuric acid, washing neutral and activating by drying at not too high temperatures.

[148] Brooks and Bacon, *J. Ind. & Eng. Chem.* 6, 623 (1914).

[149] That the fluorescent constituents are not nitrogen derivatives is indicated by the fact that 80% sulfuric acid does not remove them.

and the fluorescence of petroleum is affected by the common solvents [150] in a way entirely parallel to the findings of Kauffman [151] in the case of the diaminoterephthalic acid methyl esters. Carbon bisulfide, nitrobenzene, and aniline diminish the intensity of the fluorescence and change its original bluish green character to dull green. Amyl alcohol and petroleum ether intensify the fluorescence and enhance its bluish character. Filtration of oils through fuller's earth does not remove the fluorescent constituents appreciably. Oxidizing agents destroy the constituents in question and sun-bleached oils which have thus been subjected to air oxidation are considerably altered in this respect, usually acquiring a brownish green or muddy fluorescence.

The per cent of sulfur in the various petroleum fractions is very greatly reduced by treating with concentrated sulfuric acid, except in the case of highly unsaturated pyrolytic distillates when treated with a relatively small quantity of acid, in which case an increase in sulfur content may be observed. This is due to the formation of neutral esters of the type $\begin{matrix} RO \\ RO \end{matrix}\!\!>SO_2$. No real explanation of the removal of sulfur compounds from mineral oils by sulfuric acid can be advanced since our knowledge of the nature of these substances is so meager. Mabery and Smith [152] found that on treating a distillate from northern Ohio oil with sulfuric acid the sulfur content was reduced from 0.51% to 0.13%, and according to Robinson [153] sulfuric acid, 98% H_2SO_4, is much more effective than ordinary acid, a certain Ohio distillate containing 0.346% sulfur being thus refined to 0.05% sulfur.

The reactions of sulfuric acid and pure olefines of different types have been discussed in another section. It is there shown that the hydration of the olefines to alcohols is important only with olefines of four to eight carbon atoms and that on standing in contact with the acid the proportion of polymers increases and the yield of alcohols decreases. With olefines of ten or more carbon atoms and containing one double bond, polymerization is the principal result; in certain instances being practically quantitative. In so far as the polymerizing action of sulfuric acid on unsaturated hydrocarbons is concerned, the specific gravity and viscosity of petroleum distillates should be increased by refining. Usually a slight decrease in these

[150] Brooks & Bacon, loc. cit.
[151] *Ann.* *393*, 1 (1912).
[152] *Am. Chem. J.* *1894*, 88.
[153] *Chem. Ztg. Rep.* *1907*, 194.

values is observed after refining in this way, particularly in the case of lubricating oils. The effect of refining on the specific gravity of a number of pyrolytic gasolines, made by distillation of heavier oils under pressure of 100 to 150 pounds is indicated in the following: [154]

Specific Gravity $\frac{25°}{25°}$

Original gasoline	*After refining*	*Loss on refining, % by volume*
0.739	0.743	9.0
0.729	0.735	8.2
0.727	0.748	9.8
0.737	0.754	10.1
0.730	0.749	10.6

Such oils refined and washed in the usual way become discolored on standing a few weeks, but if they are redistilled after refining, this discoloration does not take place, at least by no means rapidly. Such a redistillation also may serve the purpose of removing the heavy oily polymers formed by the acid treatment and which are commonly believed to be objectionable constituents of gasoline when used as motor fuel or for extraction or cleaning purposes.

One of the effects of treating highly unsaturated oils with relatively *small* proportions of sulfuric acid is to form alkyl sulfuric esters which remain dissolved in the oil and are not washed out by alkali. This is shown in the following treatment of a mixture of hexenes:

SULFURIC ESTERS IN REFINED HEXENE.

Vol. Oil cc.	*Vol. H_2SO_4 cc.*	*Vol. Residual Oil cc.*	*g. SO_2 on Distillation*	*% Calc. as $(RO)_2SO_2$*
50	25	32	0.284	4.9
50	50	28	0.146	2.9
50	100	26	0.094	1.8

The concentration of the sulfuric acid employed has a marked effect upon the sulfur thus introduced, as is shown by the following results of Condrea,[155] on a Roumanian kerosene, refined by a 2% volume of acid at 20°:

Acid concentration..	90%	95%	97%	100%	5% SO_3	10% SO_3	20% SO_3
Color mm. to standard	135	175	230	290	285	270	240
SO_2.g. per 1 liter....	0.157	0.294	0.426	0.67	1.30	1.71	2.87
Sulfonic acids in acid tar	1.30	2.57	4.20	7.30	12.45	16.77	35.00

Refining with sulfuric acid at low temperatures greatly reduces the oxidizing effect of the acid, with less attendant tar and color formation.

[154] Brooks and Humphrey, loc. cit.
[155] *Rev. petrol. 1911,* 61.

It is well known that lighter colored oils are produced by operating at low temperatures, but some difference of opinion exists as to the efficiency of the refining in other respects. Zaloziecki[156] gives the following data obtained by treating a Galician kerosene with sulfuric acid, 98.94% H_2SO_4, in the proportions of 50 grams per liter of oil.

Temp. °C	*Acid Tar Grams.*	*Unused H_2SO_4*	*Sulfonic Acids Calc. as H_2SO_4*	*Acidity of Kerosene as H_2SO_4*	*Color in mm. to Match Standard*
0	61.6	47.91	1.45	0.86	193.
5	62.0	46.82	1.55	1.42	166.
10	62.5	46.53	1.65	1.56	143.
15	63.5	45.72	1.93	1.76	112.
20	64.3	44.37	2.22	2.45	89.
25	64.8	43.52	2.68	2.63	80.
30	65.2	41.87	3.72	3.65	52.
40	66.0	39.03	5.62	4.83	yellow
50	67.0	37.26	4.81	5.91	yellow

Similar results have been noted by others. Mechanical agitation during the sulfuric acid treatment results in slightly lighter colored oils than when agitated by air. Generally, in practice, little attention is paid to temperature during the sulfuric acid treatment, particularly since cooling greatly increases the viscosity of oils of the lubricating class, and thus greatly prolongs the time required for the separation of the emulsified acid tar or sludge.

Various mechanical means have been tried in the effort to increase the fineness of the emulsified oil particles, and also to decrease the time required for the tar laden acid to settle out. For the latter purpose centrifugal separation, and the addition of fine sand, infusorial earth and the like have been tried and while these methods give somewhat better oils, these methods have not been adopted in large scale practice.

Nitric acid or oxides of nitrogen in the sulfuric acid even in very small percentages,[157] e. g., .05 to 0.10 per cent, results in darker colored refined oils. Sulfuric acid made by the contact process is, therefore, much to be preferred to chamber acid, aside from the fact that the former acid is preferable on account of its greater concentration.

The higher boiling distillates, for example, lubricating oils, require very much more acid for refining than kerosene or gasoline. The chemical reactions involved are fairly well known in the latter case but the chemical character of the substances removed from lubricating

[156] *Chem. Ztg. 1911,* 1129. For data on the rise in temperature on refining oils of different types see Kissling, *Chem. Ztg. 29,* 1086 (1905); Wischin, *Petroleum 3,* 1062 (1908).

[157] Schulz, *Chem. Rev. Fett u. Harz. Ind. 20,* 82 (1913).

oils and why they react at all with sulfuric acid is not known. It is also possible that the large losses thus incurred are not necessary, that the per cent of substances present which are actually objectionable, malodorous substances, easily oxidized, color or acid forming substances, is really very small, as in the case of the lighter distillates. Naturally many other reagents have been tried, including benzensulfonic acid, phosphoric acid, zinc chloride, aluminum chloride and the like. The latter, anhydrous aluminum chloride, is the only chemical refining agent other than sulfuric acid, which has shown great promise. The tar losses in this case are very high, but the quality of the products produced, gasoline, lubricating oil or white medicinal oil, is remarkably fine.

Anhydrous aluminum chloride polymerizes olefines energetically, decomposes sulfur derivatives and naphthenic acids. Color is very effectively removed. The oils so refined are extremely stable as regards oxidation by air. Interest in this reagent for refining has recently been revived by McAfee[158] and Grey.[159] In polymerizing amylenes by aluminum chloride Aschan obtained a series of saturated hydrocarbons and believed methylcyclobutane, cyclohexane and other cyclic hydrocarbons to be present in the lower boiling fractions.

Liquid sulfur dioxide has been employed to some extent for refining kerosene, this method being based upon the marked difference in solubility of saturated and unsaturated and aromatic hydrocarbons in this solvent. With many oils the liquid sulfur dioxide method does not yield water white oils, and in such cases, refining with small proportions of sulfuric acid must be resorted to in order to get this result. The separation of the unsaturated and aromatic hydrocarbons from the paraffines is much more efficient at low temperatures, a temperature of — 12° being recommended.[160] While it is a fact that the removal of unsaturated and aromatic hydrocarbons improves the burning qualities of kerosene, and the Edeleanu process can, therefore, be considered as a rational method in this respect, there is nothing to indicate the refining value of the liquid sulfur dioxide method as regards naphthenic acids, malodorous sulfur compounds and the like. The method seems to be predicated mainly on the idea that unsaturated hydrocarbons should be removed from oils to be used as motor fuel, gasoline or naphtha solvents, lubricating oils, etc. On the other hand, there is con-

[158] U. S. Pat. 1,277,328; 1,277,092; 1,277,329.

[159] U. S. Pat. 1,193,540; 1,193,541 (essentially cracking processes). Cobb, U. S. Pat. 1,322,878; 1,322,762.

[160] See section on Physical Properties; Solubility.

siderable evidence indicating that it is possible to refine motor fuel and lubricating oils to a satisfactory degree without the large losses attendant upon the removal of the unsaturated hydrocarbons and aromatic hydrocarbons. That benzene can be satisfactorily used as a motor fuel, particularly when mixed with gasoline, or gasoline and alcohol is now generally recognized. It is probable that the unsaturated hydrocarbons themselves, as removed from pyrolytic process motor fuel by the Edeleanu method, can be employed successfully in internal combustion engines, provided the resin forming conjugated diolefines, present only in very small proportions, be removed by fuller's earth according to Hall's refining process, or an equivalent method.[161] It is also probable that transformer oils and oils intended for the lubricating of air compressors and internal combustion engines should be free from unsaturated hydrocarbons on account of the general tendency of such hydrocarbons to be readily oxidized by air. But it is possible that highly unsaturated but otherwise refined oils would prove satisfactory even in these instances. Considerable research needs to be carried out in order to determine precisely in what refining for particular purposes should consist, and to develop industrially feasible methods of refining, which would remove the objectionable constituents with little or no loss of the valuable hydrocarbons.

[161] The writer has seen test runs of an automobile engine in which pure turpentine was used as the fuel, without abnormal deposition of carbon, with excellent thermal efficiency and without carburetor difficulties. A great many of our ideas as to what the characteristics of good motor fuel should be have apparently been derived from the commercial salesman, who had a certain article to sell.

Chapter IV. The Ethylene Bond

Theory of the Ethylene Bond and Cyclic Structures

It is probably not exaggerating the relative importance of the matter to state that the chemical behavior and physical properties of the unsaturated olefine, or ethylene group, is fully as important as the well differentiated properties of condensed or benzenoid structures. The chemical properties of the ethylene structure cannot properly be indicated by a few so-called type reactions and in the following discussion it will be pointed out that all of the important chemical properties of this group may be greatly influenced by structural configuration and proximity of other groups or substituents. The properties of this group as displayed in the enol form of tautomeric compounds is not discussed at length as this material has been well presented elsewhere and it is moreover not strictly germane to the subject of hydrocarbon chemistry.

It will be of interest to examine the current theories regarding the atomic structure of such a linking. That the group $>C=C<$ is relatively unstable, or under *stress* (Baeyer), is indicated by a wealth of experimental evidence. Our conceptions or theories of such carbon "linkings" have been greatly advanced by the general hypotheses recently published by Lewis and by Langmuir. First, Lewis [1] pointed out that "a study of the mathematical theory of the electron leads, I believe (irresistibly to the conclusion that Coulomb's law of inverse squares must fail at small distances." Like Parson,[2] Lewis believed that the most stable condition for the atomic shell is the one in which eight electrons are held at the corners of a cube. As regards the carbon atom Lewis may again be quoted. "Assuming now, at least in such very small atoms as that of carbon, that each pair of electrons has a tendency to be drawn together, perhaps by magnetic force if the magnetic theory (of Parson) is correct, or perhaps by other forces which become appreciable at small distances, to occupy positions indicated by the dotted circles, we then have a model which is admirably suited to portray all of the characteristics of the carbon atom. With the

[1] *J. Am. Chem. Soc. 38,* 773 (1916).
[2] Smithsonian Inst. Public 65, 1915, p. 2371.

cubical structure it is not only impossible to represent the triple bond, but also to explain the phenomena of free mobility about a single bond which must always be assumed in stereochemistry. On the other hand, the group of eight electrons in which the *pairs* are symmetrically placed about the center gives identically the model of the tetrahedral carbon atom which has been of such utility throughout the whole of organic chemistry." Then two such tetrahedra, attached by one, two or three corners of each, represent respectively the single, double and triple bond. In the first case, one pair of electrons is held in common by the two atoms; in the second case two such pairs and in the third case, three such pairs.

According to Lewis, the triple bond represents the highest possible degree of union between two atoms. Like a double bond it may break one bond producing two *odd* carbon atoms, but it may also break in a way in which the double bond cannot, i. e., to leave a single bond and two carbon atoms (bivalent), each of which has a pair of electrons which is not bound to any other atom. The three resulting structures, in the case of acetylene, may be represented as follows, $\mathrm{H:C:::C:H}$, $\mathrm{H:\underset{\cdot}{C}::\underset{\cdot}{C}:H}$ and $\mathrm{H:\underset{\cdot\cdot}{C}:\underset{\cdot\cdot}{C}:H}$. In addition we have a form corresponding to Nef's acetylidene and such forms as may exist in highly polar media, such as the acetylidene ion $\mathrm{:C:::C:H}$.

The instability of multiple bonds, as well as the general phenomenon of ring formation in organic compounds, is admirably interpreted by the Strain Theory of Baeyer. This theory may, however, be put into a far more general form if we make the simple assumption that *all atomic kernels repel one another,* and that molecules are held together only by the pairs of electrons which are held jointly by the component atoms. Thus two carbon atoms with a single bond strive to keep their kernels as far apart as possible, and this condition is met when the adjoining corners of the two tetrahedra lie in the line joining the centers of the tetrahedra. This is an essential element of Baeyer's Theory of stress in cyclic structures. When a single bond changes to a multiple bond and the two atomic shells have two pairs of electrons in common, the kernels are forced nearer together and the mutual repulsion of these kernels greatly weakens the constraints at the points of junction. This diminution in constraint, therefore, produces a remarkable effect in increasing the mobility of the electrons. In any part of a carbon chain where a number of consecutive atoms are doubly bound there is in that whole portion of the molecule an extraor-

dinary reactivity and freedom of rearrangement. This freedom usually terminates at that point in the chain where an atom has only single bonds and in which, therefore, the electrons are held by more rigid constraints, although *it must be observed that an increased mobility of electrons (and therefore increased polarity) in one part of the molecule always produces some increase in mobility in the neighboring parts.*

"There is much chemical evidence, especially in the field of stereochemistry, that the primary valence forces between atoms act in directions nearly fixed with respect to each other." [3]

"Further evidence for the stationary electrons has been obtained by Hull, who finds that the intensities of the lines in the X-ray spectra of crystals are best accounted for on the theory that the electrons occupy definite positions in the crystal lattice."

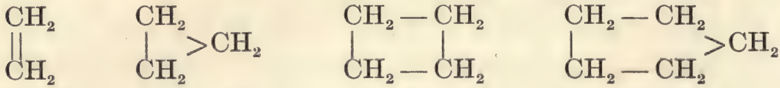
According to Langmuir's postulates carbon, atomic number six, has normally six electrons, two situated close to the nucleus or kernel as in helium, and the "four electrons in the second shell tend to arrange themselves at the corners of a tetrahedron for in this way they can get as far apart as possible." Langmuir regards the electrons in the atoms "as able to move from their normal positions under the influence of magnetic and electrostatic forces."

It should be borne in mind when reviewing the chemical properties of the ethylene bond that there is no set of reactions which infallibly characterize this group as distinguished from other unsaturated types, particularly cyclopropane derivatives. This is in accord with Baeyer's strain theory and it is probably worth while to emphasize these relationships and briefly review the theory.

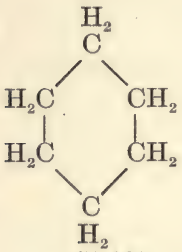
Baeyer was much impressed by the explosibility of the polyacetylene compounds and endeavored to visualize the manner in which energy could be absorbed in the formation of the acetylene bond, this energy being released as heat when such a substance explodes. From the generalization of van't Hoff and LeBel, Baeyer inferred that "the four valences of the carbon atom act in *directions* which connect the center of the sphere with the corners of a (inscribed) tetrahedron, and which form an angle of 109° 28′ with each other. The direction of the attraction (or valence) can undergo a bending or distortion, which results in a tension (Spannung) proportional to the amount of this bending." [4]

[3] Langmuir, *J. Am. Chem. Soc.* *41*, 686 (1919).
[4] *Ber.* *18*, 2269 (1885).

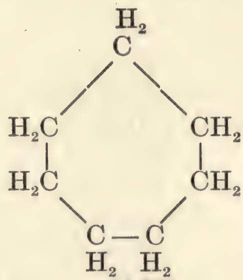
"Ethylene is the simplest methylene ring, as it may be regarded as *di*methylene." In order to bend two of these hypothetical lines of valence direction to parallel positions would require that each of the pair be deviated one-half 109° 28′ or 54° 44′ from their normal directions. In the same way the supposed deviations from the normal valence direction may be calculated for cyclopropane, cyclobutane, and so on. Ring structures containing more than five carbon atoms would require a spreading or widening of the normal angle, the angles of deviation of the simpler cyclic carbon structures being as follows:



+ 54° 44′ + 24° 44′ + 9° 44′ 0° + 44′



— 5° 16′



— 9° 33′

cycloöctane, — 12° 46′
cyclononane, — 15° 16′

Cyclopropane and its derivatives are generally not as reactive as ethylene but the ring is broken by bromine, hydriodic acid, and by hydrogen in contact with nickel at 80°. Cyclopropane is not oxidized by cold dilute permanganate. Cyclobutane is not reacted upon by bromine, concentrated hydroiodic acid or dilute permanganate solution. The ring is opened by hydrogen in the presence of nickel, forming butane at high temperature but is stable at 100°. The stability of cyclopropane and cyclobutane rings toward oxidizing agents, bromine, halogen acids, dilute sulfuric acid and the like is very greatly modified by substituent groups, just as the chemical behavior of the ethylenes is altered by different groups. Thus 1.2-dimethylcyclopropane is acted upon by 1% permanganate [5] and the hydrocarbon 1, 1, 2-trimethyl

[5] Zelinsky, *J. prakt. Chem.* 84, II, 543 (1911).

cyclopropane combines with concentrated hydrochloric acid at 100°. The derivatives

$$CH_2<\begin{array}{l}CMe_2\\ |\\ CH.CH_2CHMe_2\end{array} \qquad \text{and } CH_2<\begin{array}{l}CMe_2\\ |\\ CH.CO_2H\end{array}$$

are stable to permanganate solution but the former is hydrogenated in contact with nickel at 125° and adds hydrobromic acid very slowly.[6] Ethylcyclobutane is extremely stable, being unaffected by permanganate solution, concentrated hydrobromic acid at 100°, concentrated sulfuric acid at 25° and is only reduced by HI at 210°.

The cyclobutane derivative 1, 1, 3, 3-tetramethyl 2, 4-diethylcyclobutane

$$\begin{array}{rcl}Me_2C & — & CHC_2H_5\\ | & & |\\ C_2H_5CH & — & CMe_2\end{array}$$

is also remarkable for its stability, its chemical behavior resembling that of a saturated hydrocarbon of great inertness.[7] The acid chloride $\begin{array}{l}CH_2\\ |\\ CH_2\end{array}>CHCOCl$ is sufficiently stable to anhydrous aluminum chloride and hydrogen chloride[8] to react normally in the Friedel and Crafts synthesis to give good yields of the ketone $C_6H_5OC.CH<\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$. This fact is somewhat remarkable in view of the ease with which the cyclopropane ring in carane and sabinene and the cyclobutane ring in the pinenes is ruptured by halogen acids, by bromine and by dilute mineral acids. Wallach[9] has noted that the ketonic acid

$$CH_2<\begin{array}{l}CH.COCH_3\\ |\\ C-CH_2CO_2H\\ |\\ C_3H_7\end{array}$$

is very unstable, but the acid

$$CH_2<\begin{array}{l}CH.CO_2H\\ |\\ C-CH_2CO_2H\\ |\\ C_3H_7\end{array}$$

is very stable.

Although Baeyer's theory needs revision in the light of our present knowledge and theories of valence and atomic structure, it has passed

[6] Kishner, *J. Chem. Soc. Abs.* *1913*, I, 1163.
[7] Wedekind & Miller, *Ber.* *44*, 3285 (1911).
[8] Kishner, *J. Russ. Phys.-Chem. Soc.* *43*, 1163 (1911).
[9] *Ann.* *360*, 82 (1908); *388*, 49 (1912).

the test of usefulness and been of very great value. Experience is generally in accord with the theory and the yields in analogous reactions of synthesis indicate that in the cyclopropane, cyclobutane, cyclopentane and cyclohexane series, derivatives of cyclopropane are produced with the greatest difficulty or poorest yields, and that while cyclobutane and cyclohexane derivatives are much more easily obtained, the tendency to form cyclopentane derivatives is so pronounced that quantitative yields are frequently produced and, in fact, cyclopentane derivatives sometimes result during reactions which might be expected to yield other ring structures. As regards the relative influence of different substituent groups in such syntheses Perkin [10] states that it is clear that a useful generalization cannot be formulated until a much larger number of cyclic carboxylic acids and other derivatives have been prepared and investigated. J. von Braun [11] states that 1, 4 dihalogen alkyls and sodium malonic ester give good yields of cyclopentane derivatives but the same reaction applied to the synthesis of cyclohexane and cycloheptane compounds, from the 1, 5 and 1, 6 dihalogen derivatives, respectively, give very poor yields. The ease with which cyclohexanones are converted to cyclopentanones has been noted by Wallach [12] and the *four* carbon ring in cyclobutyldiethylcarbinol, on decomposition with loss of water, forms the *five* carbon ring 1, 2-diethylcyclopentene.[13] However, a very large number of rearrangements have been observed in which change to a system, less stable so far as the Baeyer theory and the number of carbon atoms in the ring is concerned, is brought about.[14]

J. F. Thorpe [15] and his assistants reasoned that if two valences of a given carbon atom are under strain due to ring formation, the directions of the two remaining valences would be affected, for example, the angle formed by two side chains attached to a carbon atom in a ring such as cyclohexane, would be bent from the normal 109° 28′ required by Baeyer's theory. In the case of cyclohexane these two side chains may be closer together than in a corresponding compound having an open chain structure. Their results are an interesting confirmation of the theory. Thorpe has compared the relative stability of the cyclopropane derivatives formed by the elimination of hydrogen

[10] Cf. Goldsworthy & Perkin, *J. Chem. Soc.* *105*, 2665 (1914).
[11] *Ber.* *46*, 1782 (1913).
[12] *J. Chem. Soc. Abs.* *1916*, I, 487.
[13] Kishner, *Chem. Zentr.* *1912*, I, 1001.
[14] See chapter on Rearrangements.
[15] Beesley, Ingold & Thorpe, *J. Chem. Soc.* *107*, 1080 (1915).

bromide from the monobromo derivatives of cyclohexane-1.1-diacetic acid and ββ-dimethylglutaric acid, as follows,

$$CH_2<\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}>C<\begin{matrix}CHBr.CO_2H\\ CH_2CO_2H.\end{matrix}\longrightarrow$$

$$CH_2<\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}>C<\begin{matrix}CH.CO_2H\\ |\\ CH.CO_2H\end{matrix}$$

$$\begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}CHBr.CO_2H.\\ CH_2CO_2H.\end{matrix}\longrightarrow\begin{matrix}CH_3\\ CH_3\end{matrix}>C<\begin{matrix}CH.CO_2H\\ |\\ CH.CO_2H.\end{matrix}$$

Both of the resulting acids are remarkably stable towards boiling acid permanganate solution but the chief difference observed was in their behavior to concentrated hydrochloric acid in sealed tubes at 240° under which conditions the *spiro* acid, from cyclohexanediacetic acid, is unaffected but the other, trans-caronic acid, is completely changed to terebic acid, with rupture of the ring.

The thermal measurements of Stohmann and Kleber are not in good agreement with Baeyer's theory. According to their work, the quantities of heat absorbed in the formation of similarly constituted compounds containing the cyclopropane, cyclobutane, cyclopentane and cyclohexane rings by the removal of two atoms of hydrogen from the corresponding open-chain substances, are as follows:

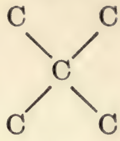
Ring	C_3	C_4	C_5	C_6
Angle of strain (Baeyer)	24.7°	9.7°	0.7°	5.3°
Heat absorbed, calories	38.1	42.6	16.1	14.3

Ingold [16] has suggested that these calculated angles of strain may not be correct and that the normal tetrahedral angle of Baeyer ($2\tan^{-1}\sqrt{2} = 109.5°$) may be modified somewhat according to the volume occupied by the four attached atoms or groups. (The distortion of the valency direction, as suggested by Ingold, has nothing in common with the theories of Guye and Brown, which refer to the effect of the size of the substituent radicles upon the asymmetry of the molecule as measured by the molecular optical activity.)

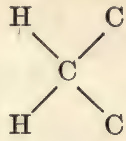
Ingold suggests that "the tetrahedron representing a carbon atom is approximately regular only when the carbon atom is attached to four atoms of a similar kind," for example, to four carbon atoms,

[16] *J. Chem. Soc. 119,* 306 (1921).

(A). However in cyclopropane, cyclobutane and the like, each carbon atom is attached to two hydrogen atoms and two carbon atoms, (B).



(A)



(B)

Since the hydrogen atom occupies a much smaller volume than the carbon atom, it is accordingly possible that in the $>CH_2$ group the two carbon atoms attached to the central one occupy more of the surrounding space than do the hydrogen atoms. If this is so, the angle between the carbon-to-carbon valencies of a polymethylene chain will not be 109.5°, as hitherto supposed, but will be some angle greater than this." Using Traubes values for the atomic volumes of carbon and hydrogen, Ingold calculates that this volume factor causes a change in the angles between each pair of carbon-to-carbon valencies in a polymethylene chain and that this angle may be nearly 6° greater than has hitherto been supposed. Employing this new angle 115.3° instead of 109.5°, Ingold calculates "by how much" the terminal carbon atoms of C_3, C_4, C_5, and C_6 rings must approach one another and obtains values more nearly in accord with the thermal results of Stohmann and Kleber.

The above stereo-chemical considerations afford an explanation of the effect of the *gem*-dimethyl group in promoting certain reactions and in other cases greatly increasing the stability of the substance. Thus, αα-dimethylbutane -αβγ-tricarboxylic acid is smoothly converted into the cyclopentanone derivative, on heating its sodium salt with acetic anhydride, but this change has not been observed with adipic acids which do not contain a *gem*-dimethyl group. The $(CH_3)_2C<$ group stabilizes certain lactones, for example, ββ-dimethylglutaric anhydride may be boiled in water for hours without change, and αββ-trimethylglutaric anhydride may be crystallized from hot water in crystals containing water of crystallization, but ordinary glutaric anhydride is easily decomposed by water.

Hückel[17] regards the heat of combustion of CH_2 as different in each polymethylene ring and points out that if the heats of combustion of these hydrocarbons are divided by the number of CH_2 groups con-

[17] *Ber.* *53 B*, 1277 (1920).

tained in the hydrocarbon concerned, then values are obtained which are much better in accord with Baeyer's theory than the older comparisons of Stohmann. In this way, the values for CH_2 in ethylene, cyclopropane, cyclobutane, cyclopentane and cyclohexane are calculated to be 170, 168.5, 165.5, 159, 158 calories, respectively.

In view of the fact that the chemical behavior of the cyclopropane group reveals a condition of unsaturation or strain (Baeyer) it is not surprising that ring closing in this case influences the physical properties of substances containing this ring complex. This will be discussed more fully in the section dealing with physical properties and constitution but it may be noted here that one of the most significant and useful properties, refractivity, is affected by the formation of the 3 carbon ring to almost the same degree as in the case of the ethylene bond, and that when the cyclopropane group occurs in a conjugated position to an ethylene bond substantially the same degree of exaltation is observed as is noticed in the case of two conjugated ethylene bonds.

Chemical Properties of Unsaturated Substances of the Ethylene Type.

Unsaturated substances of the ethylene type, e. g., substances containing one or more so-called olefine groups, are capable of a series of reactions which are very widely applicable to *nearly* all substances containing such an unsaturated group and which have come to be regarded as characteristic reactions of this type of unsaturation. These reactions are best exemplified by the addition of ozone, of halogens, particularly bromine, oxidation by potassium permanganate solution to the corresponding glycols, addition of nitrosyl chloride and oxides of nitrogen. Other reactions less widely applicable will be noted below. All of these reactions involve rupture of one of the ethylenic linkings or, in other words, one of the primary valences. In addition to these reactions, it has been noted that substituted ethylenes are capable of forming a large number of so-called molecular compounds with other substances. In these compounds the double bond is not broken and the formation of these molecular compounds is due to what is termed, for lack of a better name, "residual valence," "latent affinity," "secondary valence," and similar terms. It should be pointed out, however, that the ability to form such molecular compounds is by no means limited to unsaturated substances of the ethylene type.

Well crystallized compounds of p-tetrabromotetraphenylethylene with acetone, ether, methylethyl ketone, carbon tetrachloride, ethyl acetate and benzene, have been described. These compounds are easily decomposed to the original constituent substances. Norris [18] has submitted the following hypothesis in regard to substances of this kind.

(1). The molecular compound is formed as a result of the coming into play of latent affinities residing in an atom in each of the constituents of the compound.

(2). *All* atoms possess these latent affinities. If an atom in a compound reacts with difficulty when the latter is brought into contact with other substances, it is evident that a large part of its energy has been expended and but a little of it remains to take part in reaction. On the other hand, if the atom enters into reaction readily with other substances, it is evident that it still possesses available energy. It is probable, therefore, that such active atoms might be able to unite with atoms of a similar nature (with respect to residual energy) and form molecular compounds. A study of the literature confirms the view that compounds containing unusually active elements or groups form well characterized molecular compounds.

(3). Substances which contain inactive double bonds may form molecular compounds. In most cases direct addition of atoms or groups at the double bond leads to the formation of ordinary saturated compounds. So-called unsaturated compounds are known, however, in which the unsaturation is so slight that they will not unite with such an active element as bromine. The chemical affinity latent in the double bond is so small that it cannot hold in combination other atoms or groups linked to it by *primary* valence bonds. Many such compounds form well characterized molecular compounds. In other words, the available energy of the double bond is not enough to neutralize the energy of atoms and form a true valence bond, but is sufficient to interact with a similar small amount of energy residing in another compound. For example, p-tetrabromotetraphenylethylene $(BrC_6H_4)_2C = C(C_6H_4Br)_2$ will not react with bromine, as shown by Bauer,[19] but it does form a series of molecular compounds, as noted above. [There is apparently no way of determining whether the residual energy which makes these combinations possible in this case is really inherent in the double bond or in the bromine atom. The latter possibility suggests itself in view of the fact that tetraphenylethylene

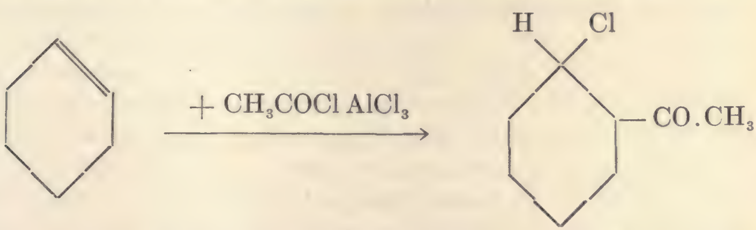
[18] *J. Am. Chem. Soc. 42,* 2086 (1920).
[19] *Ber. 37,* 3317 (1904); Hinrichsen, *Ann. 336,* 223 (1904).

dichloride $(C_6H_5)_2CCl.CCl(C_6H_5)_2$ also forms molecular compounds. B. T. B.]

The hypothesis that unsaturated hydrocarbons are able to unite with acids, by virtue of "free partial valences," to form salt-like substances was put forward and subsequently rejected by Baeyer but Kehrmann and Effront [20] have revived the hypothesis to account for the formation of two series of salts by the triphenyl methane dyes, and for the behavior of certain unsaturated ketones towards acids. For example, distyryl ketone gives mono- and *di*-acid compounds, lemon-yellow and orange-red respectively, from which it seems necessary to assume that combination can occur at one double bond in addition to the oxygen atom.

The reaction of bromine with styrene and substituted styrenes shows that replacement of one of the methylenic hydrogen atoms by an aryl group increases the reactivity to bromine slightly and this difference is further accentuated by substituting both hydrogen atoms by alkyl groups. The introduction of one halogen atom decreases the reactivity toward bromine but the effect of a CN group is even more marked, the effect of the CN and carboxyl group being of about the same order.[21]

Double compounds of ethylene and aluminum chloride have been isolated but energetic polymerization occurs with most olefines. Very little work has been done with the Friedel and Craft reaction as applied to non-benzenoid hydrocarbons. Darzens [22] found that acetyl chloride did not react with cyclohexane in the presence of aluminum chloride but with cyclohexene the saturated chloro ketone was formed.



Stannic chloride is a most efficient catalyst for this reaction. Norris and Couch [23] have recently noted that ethylene reacts with benzoyl

[20] *Ber.* *54*, 417 (1921).
[21] Reich *et al. Helv. Chim. Acta.* *4*, 242 (1921).
[22] *Compt. rend.* 150, 707 (1910). The chloride noted above may be decomposed by alkali to give the unsaturated ketone. $-HC{=}C<^{COCH_3}$
[23] *J. Am. Chem. Soc.* *42*, 2330 (1920).

chloride in the presence of $AlCl_3$ apparently in a different manner, to give phenyl vinyl ketone $C_6H_5CO.CH = CH_2$. The chloride, $C_6H_5CO.CH_2CH_2Cl$, corresponding to Darzen's product, was not observed.

There is no subject in organic chemistry to which it is more difficult to give accurate expression than the modification of the chemical behavior of certain groups or substituent atoms by other groups or atoms in the same molecule. As pointed out by Bauer the substitution in ethylene of strongly negative groups diminishes the ability of the substance to react with bromine.[24] On the other hand, the substitution of halogens or the phenyl group very markedly increases the reactivity of the ethylene group in certain other respects. Thus ethylene is polymerized only at high temperatures and pressures and in the presence of catalysts such as alumina or iron, or in the presence of very reactive substances such as anhydrous aluminum chloride or zinc chloride. On the other hand, styrene $C_6H_5CH = CH_2$, vinyl bromide, $CH_2 = CHBr$, and vinyl chloride polymerize on standing at ordinary temperatures, and rapidly under the influence of light. The enhanced reactivity of the hydrogen atoms in styrene is also indicated by the fact that this substance yields the nitro derivative $C_6H_5CH = CHNO_2$ when treated with nitric acid.[25]

That the *double bond greatly influences the reactivity* of the substituent halogen atoms is also well known. Thus vinyl bromide and vinyl chloride are remarkably stable to alkalies and in many of their reactions closely resemble chloro-benzene and bromobenzene. Advantage is taken of this unusual stability of chlorine substituted ethylenes, with respect to reactivity of the chlorine, in utilizing them as commercial solvents. For example, trichloroethylene, $CHCl = CCl_2$, is not appreciably hydrolyzed by hot water and is practically not affected by iron or copper and is therefore admirably adapted for use as a solvent in industrial apparatus made of these metals.[26] This stability of halogen derivatives of ethylene is also indicated by the commercial methods of manufacturing trichloroethylene, e. g., treating tetrachloroethane with alkali or passing over thorium oxide at 390°.[27] On treating trichlorocyclohexane with alcoholic caustic potash the prin-

[24] Perkin has called attention to the fact that the stability of cyclopropane and cyclobutane derivatives is variable within wide limits depending upon the character of the substituent groups.

[25] Recent work of Wieland, *Ber. 53*, 201 (1920), shows that ethylene reacts with a mixture of nitric and sulfuric acids (20% oleum) to give a mixture of ethylene dinitrate and B-nitro-ethyl nitrate.

[26] Gowing-Scopes, *J. Soc. Chem. Ind. 33*, 160 (1914); Crudes, *Chem. Abs. 1917*, 544.

[27] German Pat. 171,900; 206,854 (1906); 274,782 (1914).

cipal product is chlorodihydrobenzene, C_6H_7Cl, the last chlorine atom being stabilized by the adjacent double bonds.

Wohl [28] has shown that when tetramethylethylene $(CH_3)_2C = C(CH_3)_2$ is treated with n-bromoacetamide, primary addition occurs through *subsidiary valences* of the bromoacetamide and of one or both of the unsaturated carbon atoms of the olefine. Acetamide is then formed, the bromine atom taking the place of the hydrogen removed to form acetamide, the final products being acetamide and $(CH_3)_2C = C.CH_3.CH_2Br$.

Free bromine reacts energetically with the unsaturated hydrocarbons and therefore solvents are usually employed in such reactions, e. g., carbon bisulfide, carbon tetrachloride, glacial acetic acid and, less generally, alcohol or ether. The reaction is rapid and standardized solutions of bromine in acetic acid or carbon tetrachloride can often be used to titrate such hydrocarbons and determine the degree of unsaturation.[29] However, substitution of hydrogen sometimes takes place and the well-known analytical methods of Hübl, Hanus and Wijs, which are of such value with unsaturated fatty oils, cannot be relied upon to give correct results in the case of the terpenes and the higher ethylene homologues derived from petroleum.[30] Bromine addition products are sometimes crystalline solids and thus serve for purposes of identification, as in the case of butadiene, the tetrabromide [31] melting at 118°, and limonene and dipentene whose tetrabromides melt at 104°–105° and 124° respectively. The addition of halogen acids has already been referred to in the section dealing with the preparation of halogen derivatives. The addition of bromine is made use of in the analytical chemistry of rubber and a chlorinated rubber [32] has recently appeared on the market.

Hypochlorous acid reacts with ethylene bonds more readily than concentrated sulfuric acid, forming chlorohydrins. Thus ethylene reacts readily with cold dilute solutions of hypochlorous acid, and also other substances, which are inert or react only very slowly with sulfuric acid at ordinary temperatures, yield chlorohydrins, for example, cinnamic acid, allyl bromide, maleic acid and the higher ethylene homologues. Solutions of chlorine water give nearly theoretical

[28] *Ber.* *52*, B. 51 (1919).
[29] Cf. v. Soden and Zeitschel, *Ber.* *36*, 266 (1903).
[30] For description and details for carrying out these determinations see Leach, "Food Analysis," pp. 488-530, 4th Ed. Lewkowitsch, "Oils, Fats and Waxes," Vol. I, p. 393. See Faragher and Garner, *J. Ind. & Eng. Chem.* *13*, 1044 (1921).
[31] A low melting modification melting at 37.5° is also known.
[32] The product carries the trade name "Duroprene" and appears to have value as a varnish film resistant to corrosive vapors or acids.

yields of ethylene chlorohydrin but other unsaturated hydrocarbons that react energetically with chlorine also yield dichlorides. In such cases better yields of chlorohydrins are obtained by employing dilute solutions of alkali hypochlorite which yield free hypochlorous acid by hydrolysis and contain no free chlorine. Thus Walker [33] employs sodium hypochlorite in the presence of sodium bicarbonate to prepare amylene chlorohydrins (carbonic acid is a stronger acid from the ionization standpoint than hypochlorous acid). The chlorohydrins of ethylene, propylene, butylene,[34] amylenes,[35] and hexylenes are best known. Propylene and hypochlorous acid yields a mixture of the two isomers $CH_3CHOH.CH_2Cl$ and $CH_3CHCl.CH_2OH$. By the action of hydrogen chloride on propylene oxide both isomeric chlorohydrins are obtained as has been shown by an examination of their rate of hydrolysis.[36] Isobutylene and the amylenes also yield a mixture of isomeric chlorohydrins.[37] All of these simpler chlorohydrins yield alkylene oxides when treated with concentrated caustic alkali, and slow hydrolysis in the presence of sodium bicarbonate gives good yields of the glycols. The utilization of the ethylene and propylene in oil gas and petroleum still gases in this manner has recently been attempted on an industrial scale.

On heating the simpler chlorohydrins with water, aldehydes, or ketones are formed. Thus 2-chloro-3-hydroxybutane is completely converted to methyl ethyl ketone in 3 hours at 120°. Propylene chlorohydrins give acetone and propionic aldehyde and the chlorohydrin of trimethyl ethylene similarly yields methyl isopropyl ketone.[38]

The reaction of hypochlorous acid with other unsaturated substances, for example, the terpenes, unsaturated petroleum oils and fatty oils has been very little studied. Pinene yields a mixture of products,[39] among which is pinol oxide, $C_{10}H_{16}O_2$, which oxide, unlike cineol, is very easily hydrolyzed by dilute acids to a glycol. The dichlorohydrine $C_{10}H_{18}O_2Cl_2$ is also formed, the bridged ring being opened. The substance *cis*-pinolglycol-2-chlorohydrin, $C_{10}H_{17}O_2Cl$, is very stable to aqueous alkalies as is also the chlorohydrin obtained from camphene,[40] $C_{10}H_{16}HOCl$. Large proportions of chlorination

[33] U. S. Pat. 972,952; 972,954.
[34] Henry, *Bull. Acad. roy. Belg. 1906,* 523; *Compt. rend. 142,* 493; Krassuski, *Chem. Zentr. 1901,* I, 995.
[35] Carius, *Ann. 126,* 199 (1863); Umnowa, *Chem. Zentr. 1911,* I, 1278.
[36] Smith, *Z. physik, Chem. 93,* 59 (1918); Cf. Michael, *Ber. 39,* 2785 (1906).
[37] Henry, loc. cit.
[38] Krassuski, *Chem. Zentr. 1902,* II, 20.
[39] Wagner & Slawinski, *Ber. 32,* 2064; Henderson & Marsh, *J. Chem. Soc. 119,* 1492 (1921).
[40] Slawinski, *Chem. Zentr. 1906,* I, 137.

products are also formed in the case of camphene and this together with the fact that these chlorohydrins are relatively stable and are not easily converted to glycols perhaps accounts for the fact that hypochlorous acid has not become an instrument of research in this series.

The influence of constitution and the presence of substituent atoms or groups on the addition of water and behavior toward acids, or their aqueous solutions, is very pronounced. A few substances possessing double bonds, carbon to carbon, react with *water* energetically, for example, ketene $H_2C = CO$ and carbon suboxide, $OC = C = CO$, whose behavior toward water resembles that of acid anhydrides. The unsaturated hydrocarbons themselves, however, do not react with water directly although Engelder observed indications that the dehydration of alcohol to ethylene and water in the presence of alumina or kaolin, is reversible.[41]

Aqueous solutions of organic acids, particularly formic and oxalic acids, effect hydration in certain instances, for example

$$(CH_3)_2C = CH.CH_3 + H_2O \rightleftarrows (CH_3)_2.C.OH.CH_2CH_3$$

but the method is by no means general and is of no preparative value. The formation of esters of organic acids and olefines on heating or in the presence of other substances, such as zinc chloride or sulfuric acid, often gives excellent yields. Heptylene and acetic acid heated in an autoclave or sealed tube to 300° yields heptyl acetate.[42] Amylene and acetic acid react at ordinary temperatures in the presence of zinc chloride, but the yield is greatly diminished by the formation of polymers.

$$(CH_3)_2C = CH.CH_3 + CH_3CO_2H + [ZnCl_2] \begin{cases} \nearrow (CH_3)_2C(O_2C.CH_3).CH_2CH_3 \\ \searrow \text{polymers} \end{cases}$$

In most cases, better results are obtained by the method of Bertram and Walbaum, in which process the olefine is dissolved in an excess of acetic acid and a relatively very small quantity of sulfuric acid is added.[43] The presence of water greatly retards the acetylation. This reaction does not appear to have been applied industrially to the acetylation of amylenes or other olefines derived from petroleum, but

[41] *J. Phys. Chem.* 21, 676 (1917).
[42] Béhal and Desgrez, *Compt. rend.* 114, 676 (1892).
[43] *J. prakt. Chem.* 49, 7 (1894).

has been conspicuously successful in the acetylation of camphene to bornyl acetate (see Artificial Camphor). Barbier and Grignard [44] recommend benzene sulphonic acid instead of sulfuric acid to promote the reaction and state that the addition of acetic anhydride to the reaction mixture increases the yield of ester. Pinene yields mainly α-terpineol acetate.

Anhydrous oxalic acid and pinene at 120° yield bornyl oxalate and formate, which process formed the basis of the first artificial camphor process to be attempted on an industrial scale.[45] A large number of patents have been issued covering the use of other organic acids in making borneol esters. Just as hydrogen chloride containing a little moisture yields chiefly dipentene dihydrochloride, concentrated formic acid (98-99%) yields mainly terpinyl formate, the bridged ring being opened in each case.

The results of treating unsaturated hydrocarbons with sulfuric acid is of considerable interest in connection with the hydration of olefines, including the terpenes, and also the refining of petroleum distillates. The results include changes of the following nature: rearrangement, or shift in the position of the double bond, polymerization, formation of mono and dialkyl *sulfuric* esters, and hydration to alcohols.

The tendency of the olefines and substituted ethylenes to react with sulfuric acid is distinctly less than their tendency to react with bromine. Thus cinnamic and fumaric acids readily yield dibromides but are not affected by ordinary concentrated sulfuric acid at 25°. The substitution for the hydrogen of ethylene, of groups which impart a strongly electronegative character, results in decreased reactivity to sulfuric acid. Thus cinnamic and fumaric acids are inert, and dichloroethylene and trichloroethylene are only very slowly acted upon by sulfuric acid at ordinary temperatures. Allyl bromide is also more stable to sulfuric acid than is propylene. The substitution of groups which impart an electropositive character, such as methyl groups, results in greatly increased reactivity to sulfuric acid. Isobutene, $(CH_3)_2C=CH_2$ is rapidly and completely dissolved by sulfuric acid, 63% H_2SO_4, at 17°. Also tetramethylethylene $(CH_3)_2C=C(CH_3)_2$ reacts readily and completely with 77% acid at ordinary temperatures. Of the two amylenes

[44] *Compt. rend.* *145,* 1425 (1907); *Bull. Soc. Chim.* (4), *5,* 512 (1909).
[45] Thurlow, U. S. Pat. 698,761; 833,095. Carried out by the Ampere Electrochemical Co. at Niagara Falls, N. Y.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>CHCH=CH_2 \quad \text{and} \quad \begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!>C=CH_2$$

the latter dissolves more readily in 66% acid.[46] Results very closely parallel to these have been noted in the case of the reactions of amylenes and halogen acids.[47] Michael and Brunel believed that in the aliphatic hydrocarbon series the tendency to form alcohols and alkyl sulfuric esters decreases with increasing molecular weight, this result appearing to be *maximum* with the amylenes and hexylenes. With increasing molecular weight polymerization becomes the principal result, which result, however, may possibly be preceded by alcohol formation.[48] The difference in the final results may, therefore, be due in large part to the relatively greater stability of the simpler alcohols. Thus under the same conditions 3-ethylpentene (2) $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!>C=C\!<\!\begin{matrix} CH_3 \\ H \end{matrix}$ yields 72% alcohol and 12% polymers and 2-methylundecene(2) yields 97% polymers and only a trace of alcohol. Secondary octyl alcohol, octane-ol(2), treated with 95% sulfuric acid at 20° gives a yield of octene polymers $C_{16}H_{32}$ and $C_{24}H_{48}$, increasing with the time of standing. A mixture of octene(1) and octene(2) treated with sulfuric acid, with cooling, yields chiefly a mixture of the di- and tri-polymers.[49]

In a study of a series of pure unsaturated hydrocarbons Brooks and Humphrey noted that the polymers were always more stable to sulfuric acid than the parent olefines.[50] Kondakow noted a closely parallel behavior in the reaction of hydrogen chloride and isobutene and its polymers.[51] These results can be expressed in another way, e. g., unsaturated hydrocarbons are more highly polymerized, to higher boiling, more viscous polymers, by 100% sulfuric acid than by 95% acid and the latter will produce a higher degree of polymerization than 85% acid.

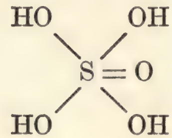
The mechanism of these changes is very obscure. It has generally been *assumed* that the alcohols, formed by treating unsaturated hydrocarbons with sulfuric acid or dilute sulfuric acid, were a result of the hydrolysis of the alkyl sulfuric esters first formed,

[46] Michael and Brunel, *Am. Chem. J.* *41*, 118 (1909).
[47] Eltekow, *Ber.* *10*, 707 (1877); Konowalow, *Ber.* *13*, 2395 (1880).
[48] Cf. Brooks and Humphrey, *J. Am. Chem. Soc.* *40*, 822 (1918).
[49] Rossolimo, *Ber.* *27*, 626 (1894).
[50] *J. Am. Chem. Soc.* *40*, 822 (1918).
[51] *J. prakt. Chem.* (2) *54*, 449 (1896).

$$\begin{array}{c} RCH \\ \| \\ RCH \end{array} + H_2SO_4 \longrightarrow \begin{array}{l} RCH_2 \\ | \\ RCHOSO_3H \end{array} + H_2O \longrightarrow \begin{array}{l} RCH_2 \\ | \\ RCHOH \end{array} + H_2SO_4$$

Thus ethyl-hydrogen sulfate *can* be hydrolyzed to give ethyl alcohol but the relative stability of this ester is indicated by the fact that a dilute solution of ethyl-sodium sulfate is hydrolyzed in 8 days at 60° only to the extent of 16 per cent.[52] The mono or acid sulfuric esters of amylenes, hexenes and heptenes are not appreciably hydrolyzed on diluting with water at ordinary temperatures and their hydrolysis in dilute solution at 100° is very slow. However, when these olefines are dissolved in cold sulfuric acid and the clear homogenous acid solution diluted with water at 0° the free alcohols are precipitated immediately in yields sometimes as high as 70 per cent of the theory. Further dilution or complete extraction of the alcohols remaining dissolved by means of an immiscible solvent causes no hydrolysis of the alkyl sulfuric esters which remain in the aqueous solution. The barium salts of these acid esters can be easily isolated by slow evaporation without appreciable decomposition. Although these alkyl sulfuric esters can be saponified by caustic alkali or hydrolyzed by prolonged boiling or steaming, they are not hydrolyzed to alcohols under the conditions which obtain in the separation of the alcohols from these sulfuric acid mixtures. Also the highest yields of alcohol are obtained when employing sulfuric acid containing water, greater yields of alcohol being obtained with 85 per cent acid than with 95 per cent or 100 per cent acid, or with benzene sulfuric acid.

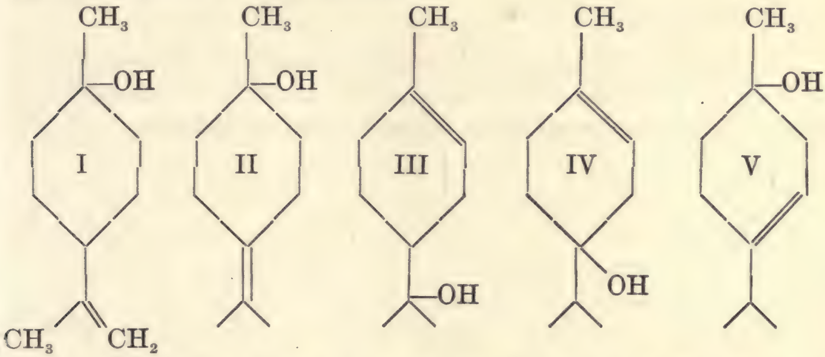
To account for these facts the theory has been proposed[53] that the addition of water to olefines with formation of free alcohols, in cold solutions, is due to reaction with the monohydrate of sulfuric acid $H_2SO_4.H_2O$, or higher hydrates. The monohydrate, or orthosulfuric acid, is usually regarded as having the constitution



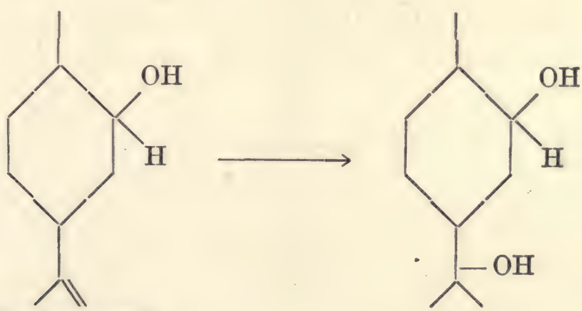
[52] Linhart, *Am. J. Sci. 35,* 283 (1913); Evans and Albertson mention that in the system $C_2H_5OH + H_2SO_4 \leftrightarrows C_2H_5H.SO_4 + H_2O$ the dilution of the mixture by titration does not cause appreciable hydrolysis. [*J. Am. Chem. Soc. 39,* 456 (1917).]
[53] Brooks and Humphrey, loc. cit.

It is practically certain that esters of this acid would have quite different degrees of stability and quite different rates of hydrolysis than the known relatively stable esters of ordinary sulfuric acid.

The hydration of pinene to terpin hydrate $C_{10}H_{18}(OH)_2.H_2O$ by dilute aqueous acids has long been known. Heating terpin hydrate with dilute sulfuric or phosphoric acids results in partial decomposition to terpineol, which process is carried out industrially. Wallach[54] has pointed out the marked effect of differences of constitution on the rate of hydration of five menthenols.



The menthenols I and II react readily with 5% sulfuric acid at ordinary temperature and III a little less rapidly. Menthenols IV and V react so much slower than I, II and III, that separation of these two groups can be effected in this way, taking advantage of the fact that the resulting terpins are not volatile with steam. Other substances having a methene group in a side chain are also very easily hydrated by dilute sulfuric acid, for example, dihydrocarveol and isopulegol,

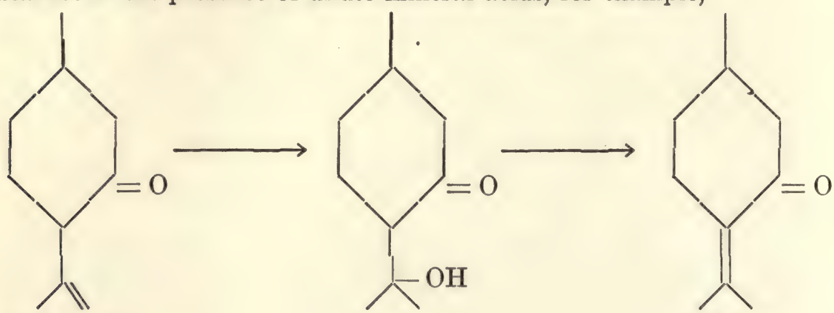


dihydrocarveol

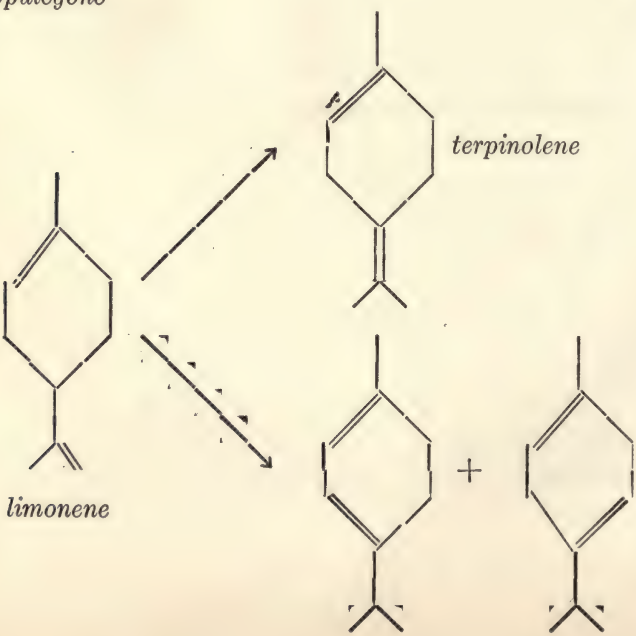
[54] *Ann.* 360, 82 (1908).

isopulegol

The facility with which such unsaturated groups are hydrated affords an explanation of the *rearrangement* of many unsaturated substances in the presence of dilute mineral acids, for example,



isopulegone *pulegone*



terpinolene

limonene

terpinenes

The rearrangement of 2-methylbutene-(3) to trimethylethylene by dilute acids is probably effected in the same manner,[55]

$$\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>CHCH=CH_2 \rightarrow \begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>CHCH<\begin{matrix}OH\\ \\CH_3\end{matrix} \rightarrow \begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>C=CH.CH_3$$

Thus when commercial amylene is hydrated by sulfuric acid, the resulting alcohol is chiefly "amylene hydrate" or dimethylethylcarbinol,[56] obtained in very pure condition from trimethylethylene,[57]

$$\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>C=CH.CH_3 \longrightarrow \begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!>C.OH.CH_2CH_3$$

Amylene and alcoholic sulfuric acid yields amyl methyl ether.[58]

Unsaturated Hydrocarbons and the Refining of Petroleum Oils.

From the foregoing section, it is clear that treatment of petroleum distillates with sulfuric acid does not completely remove the unsaturated hydrocarbons but partly polymerizes them. The polymers thus formed are not removed with the "acid sludge," but are found in the treated and washed oil. This accounts for the relatively large proportions of high boiling fractions usually obtained when a so-called cracked gasoline is refined by sulfuric acid and then redistilled.[59] When the sulfuric acid from a refining operation is diluted with water an "acid oil" is precipitated which, in the case of gasoline and kerosene, has a pronounced odor due chiefly to the alcohols present. Acid oil from the lower boiling distillates, gasoline and kerosene, contain little tarry matter. Pure mono olefines of the aliphatic series do not yield

[55] On account of this tendency of unsaturated substances to rearrange, in the presence of sulfuric or other mineral acids, the method of determining the constitution of unsaturated hydrocarbons by oxidation by chromic acid is not to be relied upon. The same consideration applies to the oxidation of certain alcohols, for example, a substance containing the group $\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!> CH.CH_2CHOH - CH_2 - R$ would undoubtedly yield a mixture of oxidation products, among which acetone derived from $\begin{matrix}CH_3\\ \\CH_3\end{matrix}\!\!> C=CH - R$ would be found.
x

[56] It will be noted that the alcohols derived from the hydration of ethylene double bonds are always tertiary or secondary alcohols; the hydroxyl group becomes attached to the more "positive" carbon atom. The industrial manufacture of alcoholic solvents from low-boiling olefines, derived from petroleum or the commercial "amylene" obtained as a by-product of the manufacture of oil gas or Pintsch gas, has been attempted. The "acid oils" obtained by diluting the sulfuric acid used in refining gasoline made by pressure distillation or similar methods also contains secondary and tertiary alcohols. Although the *tertiary* alcohol, dimethyl ethyl carbinol, boiling point 102°, is an excellent solvent for cellulose nitrate, it cannot be acetylated by ordinary methods. Like the majority of tertiary alcohols, it has a camphor-like odor.

[57] Wischnegradsky, *Ber.* *10,* 81 (1877); *Ann.* *190,* 332, 366 (1878).

[58] Reychler, *Chem. Zentr.* *1907,* I, 1125; Henry, *Bull. Acad. roy. Belg.* *1906,* 261.

[59] Cf. Brooks & Humphrey, loc. cit. The proportions of such high boiling polymers contained in a refined oil will be greater if the duration of the treating operation is prolonged, or the mixture allowed to stand.

tars with concentrated sulfuric acid at ordinary temperatures, but diolefines, particularly those containing conjugated double bonds, react very energetically with sulfuric acid, forming tars and reducing the acid. Thus highly unsaturated oils, made at very high temperatures, such as crude benzene derived from oil gas or Pintsch gas manufacture, react violently with sulfuric acid on account of the cyclohexadiene and other di-olefines contained in such oils.

When gasoline or kerosene containing unsaturated substances is refined by sulfuric acid and then redistilled, liberation of sulfur dioxide is always noted. This is present in the alkali washed oil, prior to distillation, in the form of neutral or dialkyl esters of sulfuric acid, $(RO)_2SO_2$. These esters are decomposed on heating, yielding tarry matter and sulfur dioxide. Theory indicates that refining with a minimum of sulfuric acid leads to the formation of neutral or dialkyl esters, which partly remain dissolved in the treated oil, and greater proportions of sulfuric acid favor the formation of acid or mono-alkyl esters which are readily washed out. Practice confirms this supposition; oils refined by relatively small quantities of acid contain more sulfur, in a form appearing as SO_2 on heating, than oils treated with relatively larger quantities of acid.

It is also evident from the foregoing section that the per cent by volume of unsaturated hydrocarbons contained in a certain distillate cannot be accurately ascertained by treating with sulfuric acid. The usual practice has been to determine the loss on treating with concentrated sulfuric acid but it is evident that the formation of polymers entirely destroys the quantitative character of such a determination. Such tests are of qualitative value only. The results obtained by employing sulfuric acid, Sp. Gr. 1.84 are too low, at least for gasolines and kerosene, and the results obtained when fuming sulfuric acid is employed are too high since Worstall[60] has shown, and it is a matter of common experience that fuming sulfuric acid attacks saturated hydrocarbons. Fuming sulfuric acid also sulfonates any aromatic hydrocarbons which may be present. No accurate quantitative method is now known for the determination of the percent by volume of unsaturated hydrocarbons in a mixture containing also saturated hydrocarbons (probably of various types) and aromatic or benzenoid hydrocarbons.

[60] *Am. Chem. J. 20,* 664 (1898). The original method as recommended by Krämer and Böttcher specified the use of fuming sulfuric acid. Worstall obtained yields of 30 to 40% of the sulfonic acids of n.hexane, n.heptane and n.octane. According to Markownikow naphthenes are simultaneously sulfonated and oxidized by fuming sulfuric acid. (*J. Russ. Phys.-Chem. Soc. 1892,* 141.)

Other Reactions of Olefines.

The oxidation of unsaturated hydrocarbons by air or oxygen is nearly as general a reaction as the reaction with ozone, although much less energetic than the latter. The oxidation of turpentine, and the formation of what are now recognized as peroxides, was noted by Schoenbein in his well-known studies of oxidation, hydrogen peroxide and ozone and, Berthelot like Schoenbein, wrote of ozone formation when turpentine is oxidized by air. Fudakowski[61] noted that light petroleum fractions acquired oxidizing properties similar to oxidized turpentine, when these oils were exposed to *light* and air. Kingzett[62] first proved that ozone was not present and attributed the ability of such oxidized material to effect the oxidation of other substances, to the presence of a peroxide or "hydrated oxide." A great deal of experimental work on this subject was done many years ago, but the whole matter was greatly clarified by Engler and Weissberg,[63] Bach[64] and others and the general character of the "autoxidation" of these unsaturated hydrocarbons finds close parallels in the air oxidation and resinification of rubber, particularly prior to vulcanization, the oxidation and consequent deterioration of rosin, copals and varnishes, the drying of linseed and similar oils and the deterioration of many substances by oxidation brought about by some second unsaturated substance occurring with it, for example, the destruction of cellulose fiber when in contact with lignin or rosin sizing. Engler and Weissberg showed that "the oxygen combines as molecular oxygen," and that "a peroxide is formed which may then rearrange to ordinary oxides, or may react upon other unoxidized substance." In the case of turpentine, the per cent of peroxides present after oxidation at temperatures up to 160° decreases rapidly with rising temperature, and a sample rich in peroxides, formed at low temperature, is rapidly altered by heating, the peroxides being decomposed, with further oxidation of the turpentine. As surmised by Kingzett and later shown conclusively by Clover and Richmond[65] organic peroxides are hydrolyzed by water forming hydrogen peroxide, which accounts for the many positive reactions for this substance obtained by the earlier investigators. Engler

[61] *Ber. 6,* 106 (1873).
[62] *J. Chem. Soc. 12,* 511 (1874).
[63] Vorgänge d. Autoxydation, 1904; *Ber. 31,* 3050 (1898).
[64] *Compt. rend. 124,* 2951 (1897).
[65] *Am. Chem. J. 29,* 179 (1903). The oxidizing power of old oxidized turpentine has been utilized in medicine, as an antiseptic, as an antidote for certain poisons, such as yellow phosphorus, and the more stable peroxides, such as benzoyl peroxide and benzoylacetyl peroxide studied by Clover and Richmond have been tried as antiseptics for diseases of the intestinal tract.

and Weissberg were able to isolate the peroxides of amylene, trimethyl ethylene, and hexylene in fair degree of purity.

Rupture of the ethylene bond by autoxidation has been noted in many instances, aldehydes, ketones or acids being formed; the methene group $>C = CH_2$ splits with the formation of formaldehyde or formic acid, as in the case of β-pinene, limonene[66] and β-phellandrene.[67] Willstätter sought a *catalyst,* in the hope that oxidation of unsaturated substances might be effected as easily as hydrogenation in the presence of fine nickel but, although metallic osmium appears to catalyse the reaction and cyclohexene was thus oxidized, in acetone solution, to cyclohexenol, the method has had no further extension.[68] However, the industrial use of catalysts in promoting air oxidation has long been known in the paint and varnish industry where salts or resinates of manganese, lead and cobalt are widely used. The effect of *light* in accelerating such oxidations has also long been known. In the autoxidation of styrene marked polymerization occurs, but in direct sunlight fission of the side chain occurs with the formation of benzaldehyde and formaldehyde.[69] The effect of sunlight in promoting autoxidation has been studied by Ciamician and Silber[70] whose investigations also show that oxidation under these conditions is by no means limited to substances containing an ethylene bond, but very stable ketones such as cyclohexanone and menthone are oxidized and their carbocyclic structure ruptured. Vanadium pentoxide[71] has come into vogue as catalyst for oxidizing a wide variety of substances by means of air at elevated temperatures, for example, naphthalene to phthalic acid or anhydride. These conditions are quite different from those commonly understood as autoxidation. The oxidation of olefines or saturated non-benzenoid hydrocarbons by this method has not been reported, but judging from their oxidation under very similar conditions the resulting products would probably be water, carbon dioxide, unchanged hydrocarbon and small yields of the simpler aldehydes and acids.

Closely related to the subject of autoxidation is the method discovered by Prileshajew[72] who has shown that benzoyl peroxide, $C_6H_5CO.O.OH$, combines directly, in cold neutral solvents, with sub-

[66] Blumann & Zeitschel, *Ber. 47,* 2623 (1914). For the oxidation of ethylene to formaldehyde see Ethylene, Willstätter, *Ann. 422* (1921).

[67] Wallach, *Ann. 343,* 30 (1905) ; *362,* 291 (1908) ; Kingzett has noted the corrosion of metal containers, used for turpentine, due to solution of the metal by formic acid.

[68] *Ber. 46,* 2952 (1913).

[69] Stobbe, *J. prakt. Chem. 1914,* 551.

[70] *Ber. 42,* 1510 (1909) ; *46,* 3077 (1913).

[71] Senderens employed it for oxidizing alcohols. [*J. Chem. Soc. 1913,* I, 814.] Naphthalene and benzene are also oxidizable by its aid.

[72] *Ber. 42,* 4812 (1909) ; *J. Russ. Phys.-Chem Soc. 43,* 609 (1911) ; *44,* 613 (1912).

stances containing an ethylene bond. The initial product readily decomposes to give an *oxide* of the original olefine, and these oxides are generally very easily hydrolysed to glycols. The method was applied particularly to the oxidation of linalool, geraniol, citral and citronellal. The hydrocarbons di-isobutylene, decylene and the terpenes limonene and pinene yield oxides, which may be hydrolysed to glycols, which suggests that the autoxidation of other unsaturated hydrocarbons, for example, unsaturated petroleum hydrocarbons, may lead to the formation of glycols as one of the minor products, when moisture, sufficient for hydrolysis, is present.

Probably the best known method of oxidizing the olefine group for the purpose of determining the constitution of organic substances is that of oxidizing by cold dilute potassium permanganate. Thus trimethyl ethylene gives a very good yield of the corresponding glycol,[73] and diallyl yields a hexyl erythrite. An excess of permanganate results in further oxidation of the glycol with a break in the carbon atom chain, as in the rupture of the double bond in α-pinene to form pinonic acid.[74] This break in the carbon atom structure of a substance does not *always* occur at the point at which the double bond was originally located, as has been shown in the case of carvenone and terpinenol-(4). Nevertheless, this method of oxidation and the ozone method are the most reliable means yet discovered of determining the position of ethylene bonds in organic substances.

The reaction of sulfur with unsaturated hydrocarbons has been little investigated. According to H. Erdmann[75] sulfur exists at 160° largely as S_3 or thiozone, and at this temperature he succeeded in forming a "thiozonide" of linalyl acetate $C_{12}H_{20}O_2S_3$ and was unable to obtain a derivative containing less than three atoms of sulfur. Friedmann,[76] however, isolated a compound $C_{10}H_{12}S$ by reacting upon dicyclopentadiene with sulfur.[77] By heating sulfur and turpentine together at 150° a viscous product containing 30 to 50 per cent of sulfur can be obtained.[78]

The reaction of sulfur with unsaturated hydrocarbons is of interest in connection with the vulcanization of rubber. In addition to the evidence furnished by the ozone reaction, the action of oxygen upon thin

[73] Wagner, *Ber. 21,* 1230, 3343 (1888).
[74] Baeyer, *Ber. 29,* 22 (1896).
[75] *Ann. 362,* 133 (1908).
[76] *Ber. 49,* 50, 683 (1916).
[77] Koch, German Pat. 236, 490 (1909), prepares sulfur derivatives of terpenes by heating with sulfur until hydrogen sulfide is evolved.
[78] Pratt, U. S. Pat. 1,349,909.

films of rubber indicates the presence of two double bonds for each $C_{10}H_{16}$ complex, two molecules of oxygen being combined,[79] and when treated with sulfur chloride[80] the limit of the reaction corresponds more closely to Weber's $(C_{10}H_{16}S_2Cl_2)_n$ than to Hinrichson's $[(C_{10}H_{16})_2S_2Cl_2]_n$. When pure Ceylon para, gutta-percha and extracted and purified balata are treated with 37 per cent of sulfur at 135° the final products are apparently identical and correspond to the empirical formula $(C_{10}H_{16}S_2)_n$.[81] In the ordinary hot process of vulcanization, using about 10 per cent of sulfur the first stage evidently consists in adsorption, followed by slow chemical combination,[82] and when sulfur chloride is employed adsorption followed by slow chemical combination appears to be the result.[83]

Vulcanization is essentially an increase in the degree of polymerization of the rubber and when this is effected by means of sulfur or sulfur chloride, it is probable that combination also occurs between sulfur atoms attached to different complexes or molecules, since the tendency of sulfur derivatives to polymerize is well known, as for example the thio-aldehydes. The literature on the subject of vulcanization is voluminous, and is burdened by much speculative matter which will not be reviewed here; the subject is complex and the effect of variations in mechanical treatment, and the presence of other substances, is often very marked. These effects are of great importance to the rubber industry but are not of general interest. The causes of the variability of the vulcanization of plantation *Hevea* rubber have been particularly well investigated[84] and recently a large number of substances have been investigated which promote further polymerization independently of sulfur or which greatly accelerate the vulcanization when sulfur is employed. Thus para nitrosodimethylaniline, one of the most potent accelerators, when added in amounts equivalent to 0.33 to 0.5 per cent, reduces the time required for vulcanization to about one-third that normally required and the proportion of sulfur may also be somewhat reduced. That many mineral substances, such as litharge, red lead, zinc oxide, magnesium oxide, etc., accelerate vulcanization by sulfur has long been known but a large number and variety of organic substances also function in this manner. A large number of aromatic nitro derivatives, piperidine and quinoline and

[79] Peachey, *J. Soc. Chem. Ind. 31,* 1103 (1909).
[80] Kirchof, *Kolloid Z. 14,* 35 (1914).
[81] Spence and Young, *Kolloid Z. 13,* 265 (1913).
[82] Harries, *Ber. 49,* 1196 (1916).
[83] Hinrichson, *Chem. Abs. 12,* 104 (1918); van Rossem, *Chem. Abs. 12,* 2142 (1918).
[84] Eaton & Grantham, *J. Soc. Chem. Ind. 34,* 989 (1915).

their derivatives, amines and substituted amines and ureas, have been found to have accelerating effects.[85] Barium peroxide alone has no vulcanizing effect but benzoyl peroxide does "vulcanize" in the absence of sulfur [86] but the product is markedly different from the commercial products made by the use of sulfur or sulfur chloride.[87] Dubosc has insisted that colloidal sulfur, which he assumes is formed by the interaction of hydrogen sulfide and sulfur dioxide, produced *in situ* during vulcanization, is solely responsible for the vulcanization effects. This opinion is not commonly held but it is of interest in view of the fact that a process of cold vulcanizing has recently come into use which consists in treating rubber with a mixture of these two gases, sulfur being formed in an extremely finely divided state. Reychler [88] showed that rubber takes up nearly 25 times as much sulfur dioxide as CO_2, under comparable conditions, and Peachey [89] has taken advantage of this fact in his process of vulcanization just alluded to.

The saturation of the double bonds in rubber by sulfur explains the value of "hard rubber" in handling hydrochloric, hydrofluoric and other acids. The action of sulfuric or other mineral acids upon unvulcanized rubber has been but very little investigated.

Addition of Ozone.

That ozone is capable of reacting with unsaturated hydrocarbons has been known for many years, the reaction of ethylene and ozone to form formaldehyde, formic acid and carbon dioxide having been noted by Schoenbein;[90] also the reaction between benzene and ozone was studied by Houzeau and Renard [91] but the reaction product was regarded as a peroxide rather than an ozonide. The true character of these reactions was first made clear by Harries, who pointed out that reaction with ozone in the absence of moisture gave thick viscous substances, which were very explosive, but which he was able to show by analysis consisted of products containing O_3 for each double bond present in the original substances. These ozonides can break down in two ways as follows,—

1—By reaction with water to form hydrogen peroxide and ketones or aldehydes accompanied by complete rupture of the double bond.

[85] Twiss, *J. Soc. Chem. Ind. 36,* 782 (1917); King, *Met. & Chem. Eng. 15,* 231 (1916).
[86] Ostromuislenski, *J. Russ. 47,* 1462 (1915).
[87] Twiss, loc. cit.
[88] *J. chim. phys. 8,* 617 (1910).
[89] Peachey & Shipsey, *J. Soc. Chem. Ind. 1921,* 4 T.
[90] *J. prakt. Chem. 66,* 282 (1855).
[91] *Compt. rend. 76,* 572 (1873).

$$\begin{array}{l} >\!C\text{———}C\!< + H_2O \longrightarrow >\!CO + OC\!< + H_2O_2 \\ \;\;| \qquad\quad | \\ \;\;O\text{—}O\text{—}O \end{array}$$

2—Decomposition can take place on warming or in solvents such as absolute alcohol or glacial acetic acid in the absence of water to give a peroxide and a ketone or aldehyde.

$$\begin{array}{l} >\!C\text{———}C\!< \longrightarrow >\!C\!<\begin{matrix} O \\ | \\ O \end{matrix} + OC\!< \\ \;\;| \qquad\quad | \\ \;\;O\text{—}O\text{—}O \end{array}$$

The peroxides formed as in equation (2) can often react with water to form a carboxylic acid; for example, mesityl oxide ozonide breaks down in accordance with the two schemes just shown as follows:

(a)

$$\begin{array}{l} (CH_3)_2C\text{———}CH.CO.CH_3 \\ \qquad | \qquad\quad | \qquad\qquad + H_2O \rightarrow (CH_3)_2CO + OCH.CO.CH_3 \\ \qquad O\text{—}O\text{—}O \qquad\qquad\qquad\qquad\qquad\qquad + H_2O_2 \end{array}$$

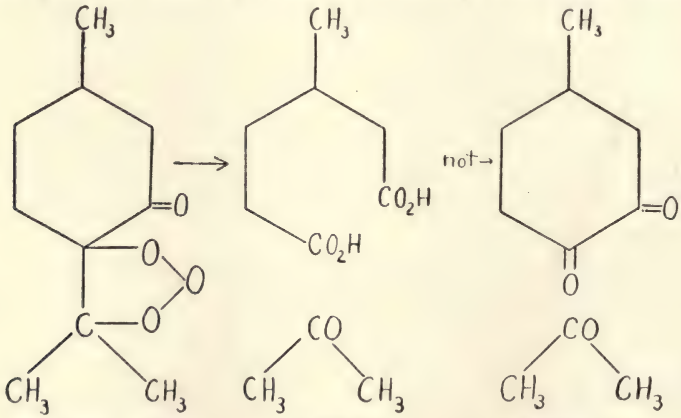
(b)

$$\begin{array}{l} (CH_3)_2C\text{———}CH.CO.CH_3 \rightarrow (CH_3)_2CO \\ \qquad | \qquad\quad | \qquad\qquad\qquad + \begin{matrix} O \\ | \\ O \end{matrix}\!>\!CH.CO.CH_3 \\ \qquad O\text{—}O\text{—}O \end{array}$$

(b_1)

$$\begin{matrix} O \\ | \\ O \end{matrix}\!>\!CH.CO.CH_3 + H_2O \rightarrow HCO_2H + CH_3COOH.$$

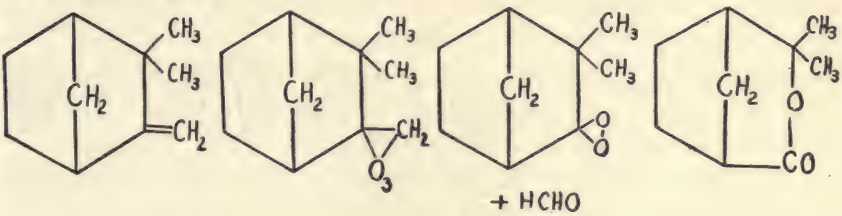
Decomposition according to (b) and (b_1) accounts for the fact that the yield of methylglyoxal is relatively small and formic and



pulegone ozonide   *β-methyladipic acid*   *1-methylcyclohexanedione-(3, 4)*

acetic acids are formed. This type of decomposition accounts for reactions which were for a time considered abnormal, for example,—pulegone ozonide[92] yields β-methyladipic acid and not the substance which would be expected from the character of the great majority of ozonide decompositions, namely, 1-methylcyclohexanedione-(3, 4)

Similarly camphene gives a little camphenilone and a relatively large yield of a lactone, whose formation is attended by rupture of the six carbon ring.[93]

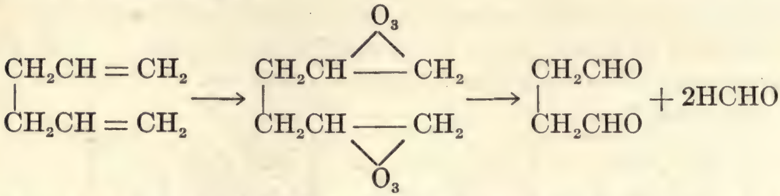


Harries regards these peroxides formed by the decomposition of ozonides as having the constitutions indicated in the above examples. Another type of peroxide is formed by the direct action of ozone upon carbonyl derivatives, aldehydes or ketones, thus nonyl aldehyde acted upon by ozone forms a labil peroxide melting at about 10°, but a more stable peroxide of the same empirical formula $CH_3.(CH_2)_7.CHO_2$ is formed by the decomposition of the ozonides of substances containing the group $CH_3(CH_2)_7CH = CHR$. This more stable peroxide melts at 73° and can readily be recrystallized.

The reaction of ethylene bonds with ozone is substantially as general a reaction as is the reaction of bromine. In fact, ozone reacts with many substances, which are commonly regarded as not having unsaturated bonds of the ethylene type, for example, benzene and naphthalene. It is of interest to note that the ethylene bond in fumaric acid, which substance is not hydrated by sulfuric acid, reacts only very slowly with ozone, but when prepared by employing very concentrated ozone the ozonide spontaneously decomposes on standing, yielding the original substance, fumaric acid. This reaction, which has been employed so successfully by Harries in the investigation of various kinds of caoutchouc, has been an outgrowth of his studies of the reaction of ozone upon mesytilene, amylene, 2.6-dimethylheptadiene-(2, 5), diallyl, and similar substances. In this connection, it should be mentioned that conjugated dienes react very energetically with ozone to

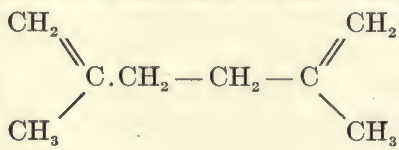
[92] Harries, *Ann.* 374, 297 (1910).
[93] Semmler, *Ber.* 42, 246 (1909); Palmen, *Ber.* 43, 1432 (1910).

form mono-ozonides, but the diozonides are formed only very slowly. Diallyl, or 1, 5 hexadiene, in chloroform solution readily gives a very explosive syrupy diozonide, which on hydrolysis yields succinic dialdehyde and formaldehyde.



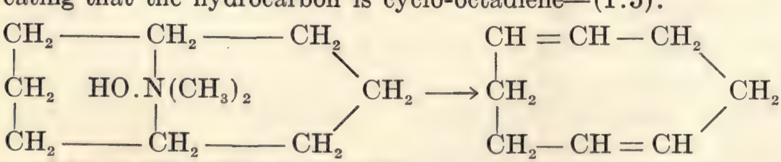
Geometrical isomers of the type of fumaric and maleic acids yield identical ozonides or rather identical hydrolytic products, which fact may serve to establish the structural similarity of such isomers.

The work of Harries on the constitution of certain unsaturated hydrocarbons has clearly shown that most of them are in reality mixtures of isomers, a fact brought out in the section on the preparation of unsaturated hydrocarbons. Thus the octadiene made by the action of methyl-magnesium iodide on succinicdiethyl ester and decomposition of the resulting glycol or its bromide was supposed to have the constitution,— $(CH_3)_2C = CH.CH = C(CH_3)_2$ but the ozone method clearly shows that this hydrocarbon is in reality a mixture chiefly consisting of the hydrocarbon

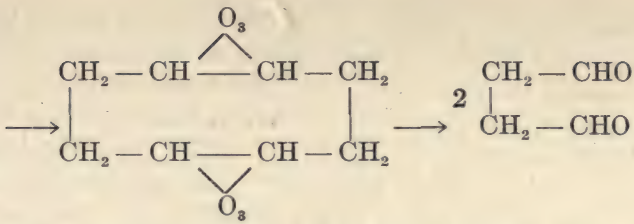


(2.5 dimethylhexadiene — (1.5)).

When the alkaloid pseudo-pelletierin is decomposed by the method of exhaustive methylation, the basic nitrogen atom is removed and a cyclo-octadiene results which Willstätter and Veraguth [94] were inclined to regard as containing a pair of conjugated double bonds. Their cyclo-octadiene polymerized with remarkable ease. Nevertheless, Harries showed that this hydrocarbon forms a diozonide which is hydrolyzed normally yielding succinic dialdehyde, and succinic acid, indicating that the hydrocarbon is cyclo-octadiene—(1.5).

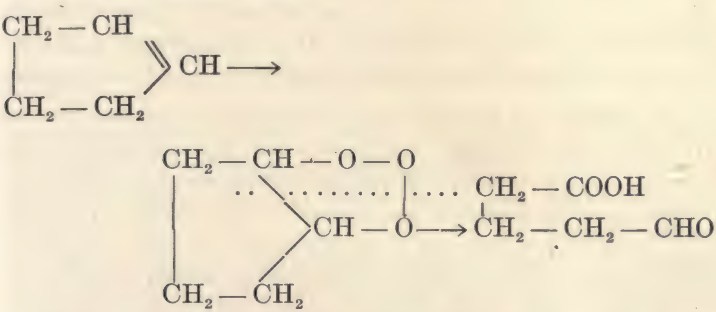


[94] *Ber.* *38*, 1975 (1905); *40*, 959 (1907).



Harries has summarized his researches on ozonides in four general articles.[95] Some of the ozonides first prepared by Harries in the earlier period of his researches were not pure and consisted apparently of mixtures derived by the addition of O_3 and also the hypothetical compound O_4 or oxozone. After passing the crude ozone-oxygen mixture through 5 per cent caustic soda and then through sulfuric acid, the gas then gave pure ozonides. Polymeric forms of ozonides have frequently been noted, an oily volatile monomolecular form having usually a sharp disagreeable odor, and polymers in the form of solid gummy, glassy or crystalline substances having little or no odor, usually being observed. Thus monomolecular butylene ozonide can be distilled in vacuo and it readily dissolves in the common solvents. The dimeric form of butylene ozonide, however, is an almost odorless gummy substance very sparingly soluble in water. Formation of ozonides at low temperatures, below 0°, favors larger proportions of the polymeric forms.

Unsaturated cyclic hydrocarbons behave toward ozone and subsequent hydrolysis generally like aliphatic olefines. Cyclopentene ozonide, $C_5H_8O_3$, is soluble in the common solvents and is smoothly hydrolyzed by water resulting chiefly in the mono-aldehyde corresponding to glutaric acid,



[95] *Ann.* *343*, 311 (1905); *374*, 288 (1910); *390*, 236 (1912); *410*, 1 (1915).

Cyclohexene ozonide is much more stable to water but on long boiling yields hexane dialdehyde and adipic acid. Limonene readily yields a mono-ozonide, the isopropenyl side chain [96] first being reacted upon, and at a much slower rate the cyclic double bond is attacked.[97]

By the ozonization of natural Hevea rubber, Harries obtained laevulinic acid and laevulinic aldehyde,[98] from which observation he concluded that Hevea rubber is a polymer of the di-isoprene, 1.5-dimethyl cyclo-octadiene-(1.5),

$$\begin{array}{llll} CH_2CH = C(CH_3) & . & CH_2 \\ | & & | \\ CH_2C = CH & \text{———} & CH_2 \\ \quad | & & \\ \quad CH_3 & & \end{array}$$

However, the real unit, which is polymerized to ring complexes an unknown number of times, is the group $-CH_2C(CH_3) = CH.CH_2-$. Artificial isoprene rubber, on treating with ozone and subsequent hydrolysis, yields succinic acid and acetonylacetone in addition to laevulinic acid and aldehyde,[99] which products could conceivably be derived from 1.6-dimethylcyclo-octadiene-(1.5).

The first work upon the treatment of petroleum distillates with ozone appears to have been done by Molinari and Fenaroli,[100] who obtained a yield of 32 per cent of an ozonide from a kerosene fraction, boiling at 295°–300°, derived from a Russian petroleum. The subject has not been pursued further but inasmuch as Harries observed that refined petroleum ether and hexane are not altogether unacted upon by ozone when used as solvents for unsaturated substances, the conclusions of Molinari that a conjugated di-olefine, $C_{17}H_{30}$, was present in the relatively large proportions indicated by the yield stated, are hardly to be accepted. Ethane is reacted upon by dilute ozone at 100°, the *initial* oxidation products being ethyl alcohol and acetaldehyde.[101] During the recent war period Harries turned his attention

[96] Prior to the researches of Harries, vanillin had been made by the action of ozone on iso-eugenol. (Otto, *Ann. d. Chim. & Phys.* [7] *13*, 120 [1898]; German Pat. 97, 620.) Better yields were, for a time, obtained by using crude ozonizing apparatus giving dilute ozone, about 1%, than when using more concentrated ozone made by improved apparatus. Harries later showed that 70% yields could be obtained by treating the ozonide with zinc dust and acetic acid (*Ber. 48*, 32 [1915].) The side chain in safrol also reacts readily, Semmler and Bartlett (*Ber. 41*, 2751 [1908]), obtaining homopiperonylic aldehyde.

[97] Critical examination of Harries' work is apt to elicit the fact that he frequently paid little attention to the history or purity of his original material and also that more definite results might often have been obtained, in the terpene series, in the hands of other well-known specialists in this field.

[98] *Ber. 38*, 1195, 3986 (1905); *46*, 733 (1913); *Ann. 406*, 173 (1914).

[99] Steimmig, *Ber. 47*, 350 (1914).

[100] *Ber. 41*, 3704 (1908).

[101] Bone and Drugman, *Proc. Chem. Soc. 20*, 127 (1904).

to the oxidation by ozone of the highly unsaturated oily distillates obtained by the low temperature carbonization of lignite. Although the method had a large scale trial in Germany during the stress of conditions imposed by the war, the yields of fatty acids obtained were very small and the project was soon abandoned.[102] Harries identified stearic, palmitic and myristic acids among the reaction products, together with relatively large proportions of simpler, water soluble acids, including formic, acetic, propionic and oxalic acids.

The reaction of unsaturated hydrocarbons with sulfur trioxide is naturally a very energetic one leading, under ordinary experimental conditions, to oxidation of the hydrocarbon and formation of SO_2. A definite reaction product is easily obtainable with ethylene, the crystalline anhydride carbyl sulfate being formed.

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2SO_3 \longrightarrow \begin{array}{l} CH_2 - SO_2 \diagdown \\ | \qquad\qquad\quad > O \\ CH_2 - O - SO_2 \diagup \end{array}$$

No further work on this reaction seems to have been done since its discovery in 1838 [103] and whether ethylene homologues can form similar derivatives (at low temperatures in a neutral solvent) is not known. The anhydride carbyl sulfate reacts energetically with water [104] to form ethionic acid, $\begin{array}{l} CH_2.SO_3H \\ | \\ CH_2.O.SO_3H \end{array}$ which substance is then rapidly hydrolyzed to iso-ethionic acid $\begin{array}{l} CH_2.SO_3H. \\ | \\ CH_2.OH \end{array}$ Sulfonic acid groups in which sulfur is bound directly to carbon, as in iso-ethionic acid, are not easily displaced and alcohols or glycols cannot be made from them by any known methods.

The propane derivative, propanol-(1) sulfonic acid-(3), is formed when allyl alcohol reacts with an alkali bisulfite,

$$\begin{array}{l} CH_2OH. \\ | \\ CH \\ \| \\ CH_2 \end{array} + KHSO_3 \longrightarrow \begin{array}{l} CH_2OH. \\ | \\ CH_2 \\ | \\ CH_2.SO_3K. \end{array}$$

[102] Ozone, as an oxidizing agent to be employed in industrial operations, is usually much too costly compared with other methods of oxidation, although its cost may be expressed largely in terms of the cost of electrical power.
[103] Regnault, *Ann.* 25, 32 (1838); Magnus, *Pogg. Ann.* 47, 509 (1839).
[104] Claesson, *J. prakt. Chem.* (2), 19, 253 (1879).

The behavior of ethylene bonds to *sulfur dioxide* and aqueous *sulfurous acid* is very different from sulfuric acid in that hydration to alcohols does not occur, but addition to form very stable sulfonic acids is frequently the result. This reaction follows the general rule that other adjacent groups exert a very great influence upon the reactivity of the unsaturated bond. Anhydrous sulfur dioxide has not been shown to react with unsaturated hydrocarbons, although the very marked solubility of such hydrocarbons in liquid sulfur dioxide and the completeness with which they may be extracted from paraffine hydrocarbon mixtures, as in the Edeleanu refining process, might be considered as an indication of the formation of such labil compounds. When solutions of amylenes or butylene in sulfur dioxide are subjected to the action of heat and light, amorphous hornlike solids are formed,[105] the butylene compound having the composition $(C_4H_8SO_2)_n$, and when the conjugated diene, isoprene, is allowed to stand two days in liquid sulfur dioxide a crystalline substance $C_5H_8SO_2$, is formed.[106]

Sulfonic acid derivatives of sabinene, sabinol and pulegone are formed when SO_2 is passed into their cooled alcoholic solutions [107] but the formation of sulfonic acid derivatives has been most frequently observed in cases where the ethylene bond is adjacent to a carbonyl group, $>CH=CH-\underset{\underset{O}{\|}}{C}-$. Thus acrolein [108] and crotonic aldehyde [109] react with sodium bisulfite normally so far as the aldehyde group is concerned but the ethylene bonds react also, to form stable sulfonic acid derivatives, which are not affected by treating with alkali. The aldehyde group generally reacts more readily with bisulfite than the ethylene bond and advantage is taken of this fact in isolating unsaturated aldehydes, such as citral and citronellal, from mixtures containing them. Citral contains two double bonds, one of them adjacent to the aldehyde group, and both ethylene bonds may react yielding the stable disulfonic acid salt, $C_9H_{17}.(SO_3Na)_2.CHO$, from which citral cannot be regenerated. When cold neutral sodium sulfite is employed and the alkali, formed by the reaction, is neutralized as fast as formed,

$$C_9H_{15}.CHO + 2Na_2SO_3 + 2H_2O \rightarrow C_9H_{15}(SO_3Na)_2CHO + 2NaOH$$

[105] Mathews and Elder, *J. Soc. Chem. Ind.* *1915*, 670.
[106] de Bruin, *Chem. Abs.* *9*, 623 (1915).
[107] Wallach, *Nachr. Wiss. Ges. Goettingen.* *1919*, 321.
[108] Müller, *Ber.* *6*, 1442 (1873).
[109] Haubner, *Monatsh.* *12*, 546 (1891).

then an *unstable* dihydrosulfonate is formed from which citral is easily regenerated.[110] Citronellal contains only one double bond and this is far removed from the aldehyde group and accordingly less reactive. Under the conditions just described citronellal is not reactive;[111] with cold concentrated bisulfite, in the presence of sodium bicarbonate, the aldehyde group only reacts, and normally, but when *warmed* with an excess of bisulfite (containing a little sulfite) the stable sulfonate is formed.[112]

$$\text{citronellal} \xrightarrow{\text{cold}} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2CH\!<\!\begin{matrix} OH \\ OSO_2Na \end{matrix}$$

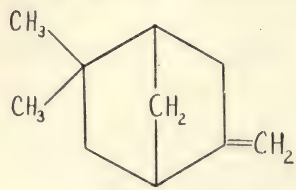
$$\text{citronellal} \xrightarrow{\text{hot}} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\displaystyle SO_3Na}{\underset{|}{C}}-CH_2.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2CH\!<\!\begin{matrix} OH \\ OSO_2Na \end{matrix}$$

cannot be regenerated.

Nitrosyl chloride has been a most useful reagent in the investigation of the terpenes but has not been used in the investigation of unsaturated hydrocarbons derived from petroleum, although the first thorough study of the addition of nitrosyl chloride to olefines was carried out with amylene.[113] When Wallach first undertook the study of the terpenes the literature had become confused with a variety of names for hydrocarbons which were not clearly differentiated, one from another, and the names adopted usually referred to various particular sources. The reaction with nitrosyl chloride, which had been discovered by Tilden and Shenstone,[114] proved to be a most valuable reagent for the preparation of characteristic crystalline derivatives of these unsaturated hydrocarbons and the multiplicity of names began to diminish as the identity of differently named terpenes was established. The addition products formed by the reaction of these hydrocarbons with nitrogen trioxide and nitrogen tetroxide also proved useful in this connection. Crystalline tetrabromides, dihydrochlorides, etc., also assisted in this work of identification and "citrene," "hesperidene," and "carvene," for example, were shown to be identical and are known as limonene.

[110] Tiemann, *Ber.* *31,* 3306, 3315 (1898).
[111] Tiemann, *Ber.* *32,* 816, 818 (1899).
[112] Tiemann, *Ber.* *31,* 3306 (1898).
[113] Wallach, *Ann.* *245,* 246 (1888).
[114] *J. Chem. Soc.* *1877,* I, 554.

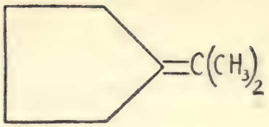
Among the simpler olefines the ability of olefines to combine with nitrosyl chloride increases with molecular weight (or introduction of the "positive" methyl groups): ethylene forms only ethylene chloride, and propylene forms both the dichloride and nitrosochloride.[115] As indicating the variety of ethylene types which form nitrosochlorides, the following may be mentioned, trimethyl and tetramethyl ethylene, cyclohexene, methene derivatives $R_2C = CH_2$, and also hydrocarbons having a semicyclic double bond and a side chain, as $(CH_2)_x{<}\begin{matrix}CH_2\\ \\CH_2\end{matrix}{>}C = CH.R$. Unsaturated hydrocarbons having the groups $>C = CH_2$, and $-CH = CH_2$, do not *usually* yield crystalline nitrosochlorides: [116] the type $R_2C = CHR$ usually does yield crystalline nitrosochlorides.[117] The terpene, β-fenchene



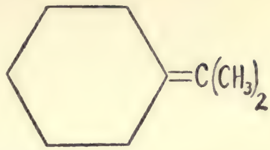
forms a crystalline nitrosochloride and Wallach has obtained such crystalline derivatives from other hydrocarbons whose double bond is similarly situated.[118]

The crystalline nitrosochlorides, nitrosites and nitrosates are generally bimolecular [119] and hence called *bis*-nitrosochlorides, *bis*-nitrosites and *bis*-nitrosates, but in solution many [120] of these derivatives are blue in color and are monomolecular. Many of the nitrosochlorides, in monomolecular form, are volatile with steam without decomposition; for example, the blue modifications derived from the hydrocarbons,[121, 122]

[115] Tilden & Sudborough, *J. Chem. Soc. 63,* 479 (1893).
[116] Meyer, "Analyse & Konstitutioniren. org. Verb," Ed. 2, Berlin, 1909, p. 939.
[117] Weyl, "Die Methoden d. org. Chemie," II, 639 (1911).
[118] *Ann. 347,* 322 (1906); *365,* 267 (1909).
[119] Baeyer, *Ber. 28,* 641, 650, 1586 (1895); *29,* 1078 (1896).
[120] Wallach & Sieverts, *Ann. 306,* 279 (1898), *332,* 309 (1904), showed that pinol nitrosochloride may exist in a *colorless* monomolecular form.
[121] Wallach, *Ann. 353,* 308 (1907); *396,* 280.
[122] The preparation of nitrosochlorides is best carried out by dissolving the hydrocarbon in an equal volume of glacial acetic acid, adding one volume of ethyl nitrite, cooling to 10°, and then adding one-third volume of concentrated hydrochloric acid. In most cases, where a crystalline nitrosochloride is possible, an abundant crystalline deposit of the nitrosochloride forms in a few minutes. Acetone is generally the best solvent for recrystallizing these derivatives. Nitrosobromides are also easily prepared but are less stable than the corresponding chlorides: 5cc tetramethyl-ethylene and 5cc ethyl nitrite, cooled to 0° C and treated with 5cc concentrated HBr solidifies in a few minutes to the solid bisnitrosobromide.



and



The value of the nitrosochlorides has been chiefly their ready conversion to oximes, from which ketones may be made, and to other more stable substances suitable for identification purposes, for example, condensation with benzylamine. All three types of nitroso derivatives may be converted into the isomeric oximes by carefully warming with alkalies,

$$\begin{array}{l} (CH_3)_2C - Cl \\ \quad\;\; | \\ CH_3 - CH.NO \end{array} \longrightarrow \begin{array}{l} (CH_3)_2C.Cl \\ \quad\;\; | \\ CH_3 - C = N.OH \end{array}$$

It has been proposed to utilize the reaction with nitrogen tetroxide in determining the constitution of olefines, since the addition product $RCH.NO_2.CHNO_2.R$, is split by heating with concentrated hydrochloric acid to give fatty acids.[123]

Ammonia and aliphatic amines react with the ethylene bond in certain instances where the very reactive ethylene-carbonyl group $>CH = CH - \underset{\underset{O}{\|}}{C} -$ occurs, as in mesityl oxide,[124]

$$(CH_3)_2C = CH.CO.CH_3 + NH_3 \longrightarrow (CH_3)_2C\begin{array}{l} \diagup NH_2 \\ \diagdown CH_2COCH_3 \end{array}$$

Vinyl chloride, which polymerizes on standing but is quite stable to sulfuric acid, reacts with ammonia to give ethylenediamine,[125]

$$CH_2 = CHCl + 2NH_3 \longrightarrow NH_2.CH_2CH_2NH_2HCl$$

The unsaturated hydrocarbons themselves are not reactive to ammonia or amines. The ethylene-carbonyl group is also reactive to hydroxylamine in a fairly large number of substances. Allyl ketones, $CH_2 = CH.CH_2COR$, react normally to give oximes but the ethylene bonds in propenyl and vinyl ketones also react,[126]

[123] Jegorow, *J. prakt. Chem. 86*, 521 (1912).
[124] Sokoloff, *Ber. 7*, 1387 (1874); Kohn, *Monatsh. 25*, 135 (1903); Blaise & Maire, *Compt. rend. 142*, 215 (1906).
[125] Engel, *Compt. rend. 104*, 1621 (1887).
[126] Blaise, *Compt. rend. 138*, 1106 (1904); *142*, 215 (1906).

$$CH_2 = CH.COR \longrightarrow NH.OH.CH_2CH_2C\begin{array}{l} \diagup R \\ \\ \diagdown\!\!\diagdown N.OH \end{array}$$

The ethylene-carbonyl group also reacts with aniline, phenyl hydrazine, urea, semicarbazide, mercaptans, hydrogen sulfide, hydrocyanic acid, malonic and acetoacetic esters.

$$\textit{aniline}\,[127] + RCH = C<\begin{array}{l} CO_2R \\ CO_2R \end{array} \longrightarrow \begin{array}{l} RCH - CH<\begin{array}{l} CO_2R \\ CO_2R \end{array} \\ \;| \\ NH.C_6H_5 \end{array}$$

$$\textit{urea}\,[128] + \begin{array}{l} CH.COOH \\ \| \\ CH_2 \end{array} \longrightarrow \begin{array}{lcl} NH - CO - CH_2 \\ | \qquad\qquad\quad | \\ CO - NH - CH_2 \end{array}$$

$$\textit{semicarbazide}\,[129] + (CH_3)_2C = CHCOCH_3$$

$$\longrightarrow \begin{array}{l} (CH_3)_2C - CH_2.\overset{CH_3}{\overset{\diagup}{C}} = N.NH.CO.NH_2 \\ \qquad\;\; | \\ \qquad NH.CO.NH.NH_2 \end{array}$$

$$\textit{ethyl mercaptan}\,[130] + (CH_3)_2C = CH.\begin{array}{l} CO \\ \;| \\ CH_3 \end{array}$$

$$\longrightarrow \begin{array}{l} (CH_3)_2C - CH_2C<\begin{array}{l} SC_2H_5 \\ SC_2H_5 \end{array} \\ \qquad\;\; | \qquad\quad\;\; | \\ \qquad SC_2H_5 \quad CH_3 \end{array}$$

$$\textit{hydrogen sulfide}\,[131] + \text{carvone} \longrightarrow (C_{40}H_{14}O)_2H_2S$$

$$\textit{hydrocyanic acid}\,[132] + (CH_3)_2C = CH.COCH_3$$

$$\longrightarrow \begin{array}{l} (CH_3)_2C - CH_2COCH_3 \\ \qquad\;\; | \\ \qquad\; CN \end{array}$$

[127] Blank, *Ber. 28,* 145 (1895).

[128] Fischer & Roeder, *Ber. 34,* 3751 (1901).

[129] Important in connection with the use of semicarbazid for the identification of such ketones; citronellal and two molecules of semicarbazid gives the crystalline semicarbazino-semicarbazone immediately. Cf. Rupe, *Ber. 36,* 4377 (1903); Semmler, *Ber. 41,* 3991 (1908).

[130] Posner, *Ber. 35,* 799 (1902); *37,* 502 (1904).

[131] Cf. Wallach, *Ann. 279,* 385 (1894); *343,* 32 (1905); mesityloxide and the hydrocarbon menthene also form compounds with H_2S.

[132] Lapworth, *Jour. Chem. Soc. 85,* 1214 (1904).

$$\textit{acetoacetic ester}^{133} + CH_2 = CH.CO_2R \longrightarrow \begin{array}{l} CH_3COCH.CO_2R \\ \quad | \\ \quad CH_2 - CH_2.CO_2R \end{array}$$

The above reactions cannot be said to be general reactions even for α, β-unsaturated ketones or acids (the "ethylene-ketone" group), and none of them have so far been found applicable to hydrocarbons. In fact, until the mechanism of such reactions, and the part played by the carbonyl group, is understood, it is questionable whether this last group of reactions should really be considered as reactions of the unsaturated bond; it would be more correct to consider them as reactions of the $>CH = CH - \underset{\underset{O}{\|}}{C} -$ or "ethylene-carbonyl" group. These considerations apply also to the hydrolytic rupture of the ethylene bond of this group which is noted when many substances, for example, mesityl oxide, citral [134] and pulegone, are treated with dilute alkalies or mineral acids, thus

$$(CH_3)_2C = CH.CO.CH_3 \xrightarrow{+H_2O} (CH_3)_2CO + CH_3COCH_3$$

$$\begin{array}{c} (CH_3)_2C = CH.CH_2CH_2\underset{\underset{CH_3}{|}}{C} = CH.CHO \\ \text{citral} \end{array}$$

$$\xrightarrow{+H_2O} (CH_3)_2C = CH.CH_2CH_2\underset{\underset{CH_3}{|}}{C} = O$$

$$+ CH_3CHO$$

Metallic sodium has been observed to combine directly with unsaturated hydrocarbons [135] only in a few cases where a negative group is present, as in stilbene, $C_6H_5CH = CH_2$. Metallic sodium in a very finely divided or colloidal form is employed for the purpose.

Preparation of Olefines.

As regards the preparation of olefine hydrocarbons, it may be pointed out that most methods of preparation yield a mixture of isomers

[133] Vorländer, *Ann.* *294*, 317 (1897).

[134] Verley, *Bull. soc. chim.* (3), *17*, 175 (1897). Effected best by heating with potassium carbonate; pulegone may be hydrolyzed by heating with water in an autoclave. Wallach, *Ber.* *32*, 3388 (1899).

[135] Schlenk, Appenrodt, Michael & Thal, *Ber.* *47*, 473 (1914).

and that often when a single product is theoretically probable a mixture of isomers results owing to rearrangement. Thus Eltekow[136] showed that isobutyl alcohol or the corresponding halides decompose to give a mixture of three butylenes,

$$\begin{array}{l}\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH_2X \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH_2\\ \qquad\qquad\qquad\qquad\quad CH_3CH=CH.CH_3\\ \qquad\qquad\qquad\qquad\quad CH_3CH_2CH=CH_2\end{array}$$

Haber[137] showed that on heating normal hexane to 600° to 800°, it is decomposed, methane and amylene being found among the products formed and assumed that the amylene was alpha amylene, as expressed by the equation,

$$C_3H_7.CH_2CH_2CH_3 \longrightarrow C_3H_7CH=CH_2+CH_4$$

But, as indicated in the case of the butylenes, olefines of the type $RCH=CH_2$ are prone to rearrangement under the influence of heat. Thus the amylene $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.CH=CH_2$ rearranges under the influence of heat, or mineral acids, to trimethylethylene,

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C=CH.CH_3$$

Noorduyn[138] has made a study of the constitution of the olefines formed by heating barium fatty acid salts with sodium ethoxide or methoxide. Very little work of this kind, critical examination of the constitution of acyclic olefines, has been done. Five methods have been used to determine the constitution of unsaturated substances.

(1) The method of Varrentrap; fusion with caustic potash which causes a change of position of the double bond toward the carboxyl group (of fatty acids).

(2) Oxidation by potassium permanganate, in which method 1:2 glycols are former as intermediate products.

(3) Beckmann's transposition, in which method the formation of the dibromide is the first step.

[136] *Ber.* *13*, 2404 (1880) ; Cf. Nef, *Ann.* *318*, 1 (1901).
[137] *Ber.* *29*, 2691 (1896).
[138] *Rec. trav. chim.* *38*, 317 (1919).

(4) Jegorow's method based upon the addition of N_2O_4 to the double bond.

(5) Harries' method consisting in reaction with ozone and hydrolysis of the resulting ozonide.

Noorduyn used the ozonide method. Examination of the decylene made by heating the barium salt of undecylenic acid with sodium ethoxide and hydrolyzing the ozonide of the hydrocarbon yielded formaldehyde, acetic, propionic, butyric, valeric and hexylic acids showing that the hydrocarbon is a mixture of isomers. Similarly the heptadecylene, from oleic and elaidic acids and sodium methoxide was shown to be a mixture of isomeric hydrocarbons. Nonylenic acid, from oenanthole and malonic ester, yielded a mixture of octylenes and "β-octylene," boiling-point 124°–126° from secondary octyl alcohol was also shown to be a mixture.

Primary alkyl iodides or alcohols invariably yield a mixture of hydrocarbons, as a critical examination of the physical properties of the hydrocarbons described in the literature as having been prepared in these ways, shows. Thus Morgan and Schorlemmer [139] prepared a hexene, boiling-point 68° to 70°, from a monochlorohexane and Zelinsky and Przewalski [140] heated n-hexyl iodide with quinoline and obtained a liquid mixture boiling from 35° to 67°. On oxidizing the fraction boiling from 63.5° to 65° they obtained a mixture of butyric and valeric acids indicating that this hexene fraction was probably a mixture of the α and β-isomers. Van Beresteyn [141] also obtained a hexene boiling at 67.7° to 68.1° by decomposing n-heptyl alcohol by heating in contact with nickel at 220°.

$$CH_3(CH_2)_3CH_2CH_2CH_2OH \rightarrow CH_3(CH_2)_3CH = CH_2\ ? + CO + 2H_2$$

However, von Braun [142] obtained a hexene, by gently heating n-hexyl trimethyl ammonium hydroxide, which showed a boiling-point of 62° to 63° and which he regarded as α-hexene, although he was unable to prove the constitution of it on account of the small quantity made. Brooks and Humphrey [143] confirmed the character of von Braun's α-hexene by synthesizing it by means of a reaction which had been applied by Tiffeneau [144] to the synthesis of allyl derivatives of ben-

[139] *Ann.* **177**, 305 (1875).
[140] *Chem. Zentr.* **79**, II, 1854 (1908).
[141] *Ibid.* **1911**, II, 1017.
[142] *Ann.* **382**, 22 (1911).
[143] *J. Am. Chem. Soc.* **40**, 833 (1918).
[144] *Compt. rend.* **139**, 481 (1904).

zene.[145] They treated n-propyl magnesium bromide with allyl bromide, the reaction taking place smoothly at room temperature.

$$C_3H_7MgBr + BrCH_2CH = CH_2 \longrightarrow C_3H_7CH_2CH = CH_2 + MgBr_2$$

Iso-α-heptene, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH.CH_2CH_2CH = CH_2$ and iso-α-octene were also made in a similar manner. This reaction is undoubtedly applicable to the preparation of a large number of alpha olefines of this series.

Pure olefines of other types may be prepared in certain cases by making use of the *symmetry* of the parent alcohol or halide. For example, the tertiary alcohol triethylcarbinol readily yields pure γ-ethyl-β-pentene (3-ethyl pentene-2).

$$\begin{array}{ccc} & C_2H_5 & \\ & | & \\ C_2H_3 - & C & - OH \\ & | & \\ & C_2H_5 & \end{array} \longrightarrow \begin{array}{l} \quad\;\; C_2H_5 \\ \quad\quad\; | \\ C_2H_5C \\ \quad\quad\; \| \\ \quad\;\; CH.CH_3 \end{array}$$

and δ-iodo heptane, $C_3H_7 - CHI - C_3H_7$, by virtue of its symmetry, yields pure γ-heptene when decomposed by caustic alkali.

The simpler primary alkyl chlorides and bromides on treatment with caustic alkali in methyl or ethyl alcohol yield chiefly methyl or ethyl ethers but alkyl iodides of five or more carbon atoms, particularly secondary and tertiary derivatives, yield olefines almost quantitatively.[146]

Organic bases, aniline, quinoline and the like have frequently been employed to remove halogens with success. Tertiary halides, like tertiary alcohols, are easily decomposed and Klages [147] has employed pyridine for tertiary chlorides. Decomposition of alkyl halides by heat is usually attended by rearrangements and often with rupture of the carbon structure, and, in some cases, by condensation or polymerization, but many substances catalyze this decomposition of the halides, so that lower temperatures may be employed and subsequent changes of the olefines may be minimized. Nearly quantitative yields of ethylene

[145] Austerweil later synthesized isoprenes in a similar way, treating vinyl-magnesium bromide with beta-chloropropylene,

$$Mg\begin{matrix} \diagup CH = CH_2 \\ \diagdown Br \end{matrix} + CH_3C\begin{matrix} \diagup Cl \\ \diagdown\!\diagdown CH_2 \end{matrix} \longrightarrow MgBrCl + CH_3C\begin{matrix} \diagup CH = CH_2 \\ \diagdown\!\diagdown CH_2 \end{matrix}$$

J. Chem. Soc. Abs. *102*, 525 (1912).

[146] Nef, *Ann.* *309*, 126 (1899); *318*, 1 (1901).

[147] *Ber.* *35*, 2633 (1902).

may be obtained from ethyl chloride by heating in contact with barium chloride and chloropentanes can be decomposed to amylenes in this manner.[148] A large number of processes for the decomposition of bornyl chloride to camphene have been described in connection with the synthesis of camphor. Bornyl chloride is remarkably stable and most of the successful reactions are carried out within the range 160° to 190°. Usually an alkaline substance or mixture is sought which will dissolve the bornyl chloride forming a homogenous reaction mixture and patented methods refer to the use of sodium phenolate, sodium soaps such as oleate, linoleate, etc., sodium acetate in acetic acid, aniline, quinoline, etc. Zinc chloride catalyzes the decomposition of bornyl chloride but rapidly polymerizes the camphene formed.

Certain olefines are often most readily made by the decomposition of halogenated, hydroxy or unsaturated fatty acids but these methods are by no means generally applicable. Pure β-butylene is easily made from bromotiglic acid by heating with soda in aqueous solution.[149]

$$CH_3CHBrCH\begin{matrix} \diagup CH_3 \\ \\ \diagdown CO_2Na \end{matrix} \longrightarrow CH_3CH = CHCH_3 + CO_2 + NaBr$$

The β-halogen derivatives of the fatty acids are decomposed very easily by alkalies and the resulting unsaturated acids frequently lose CO_2 on heating or distilling to give an olefine. β-bromoisobutyric acid is quantitatively decomposed by aqueous barium hydroxide to methyl acrylic acid,

$$\begin{matrix} CH_3 \diagdown \\ \\ CH_2Br \diagup \end{matrix} CH.CO_2H \longrightarrow \begin{matrix} CH_3 \diagdown \\ \\ CH_2 /\!\!/ \end{matrix} C.CO_2H$$

and α-bromobutyric acid, considerably more stable, also yields methyl acrylic acid by treating with 25% caustic soda.[150] Normal β-bromo fatty acids on heating with water, dilute alkali, or by destructive distillation, yield more of the α-β-unsaturated acid than the β-γ-unsaturated acid. Wallach [151] has made use of the instability of the β-hydroxy acids to

[148] Badische, German Pat. 255,519, *J. Chem. Soc. 104,* 438 (1913); German Pat. 268,100, *Chem. Zentr. 1914,* I, 308; Sabatier & Mailhe, *J. Chem. Soc. 104,* 330 (1913); Braun and Deutsch, *Ber. 45,* 1271 (1912).

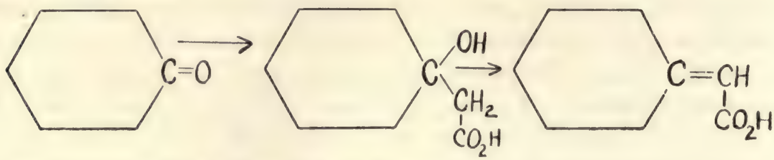
According to Mathews, Bliss and Elder, the decomposition of alkyl halides within the range 100°-700° is catalyzed by water, either in the presence or absence of other catalysts. Brit. Pat, 16,828 (1912); 17,234 (1912).

[149] Pagenstecher, *Ann. 195,* 112 (1879).

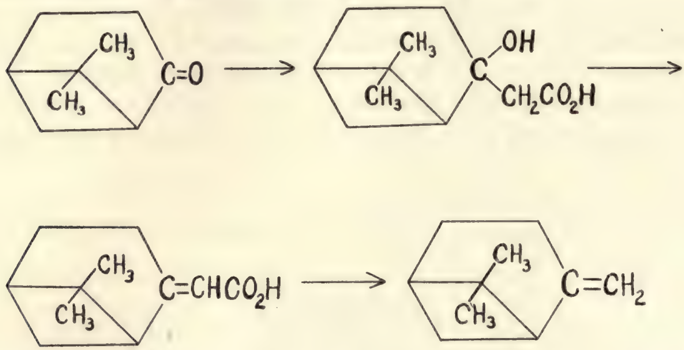
[150] Engehorn, *Ann. 200,* 68 (1880); Bischoff, *Ber. 24,* 1041 (1891).

[151] *Ann. 365,* 257 (1909).

synthesize olefines containing the methene group. Using the method of Reformatsky of condensing ketones or aldehydes with bromoacetic ester by means of zinc, Wallach proceeded as indicated by the following reactions, the hydroxy acids being dehydrated by heating with acetic anhydride.



and from nopinone β-pinene was synthesized,



Tertiary alcohols decompose so readily that they are difficult to acetylate. Glacial acetic acid at 150° to 155°, or acetic anhydride containing a little zinc chloride, or sulfuric acid, yields chiefly unsaturated hydrocarbon. Thus trimethyl carbinol yields isobutylene,[152] diethylpropylcarbinol yields an octene,[153] etc.

Primary and secondary alcohols of high molecular weight may be converted to olefines by the method of Krafft,[154] i. e., treating with palmityl chloride and distilling the palmitic ester slowly at ordinary pressure. In the terpene series the method developed by Tschugaeff [155] consisting in heating the methylxanthogenate ester of the alcohol, has given excellent results. Very little heat is usually required and the probability of rearrangement or decomposition is greatly lessened; in fact, the methylxanthogenate esters of *tertiary* alcohols, if formed, decompose spontaneously at ordinary temperatures. Henderson [156] pre-

[152] Menschutkin, *Ann. 197*, 204 (1879).
[153] Mason, *Compt. rend. 132*, 483 (1901); Henry, *Compt. rend. 144*, 552 (1907); *147*, 1260 (1908).
[154] *Ber. 16*, 3020 (1883).
[155] *Ber. 32*, 3332 (1899).
[156] *J. Chem. Soc. 97*, 1620 (1910); *99*, 1903 (1911).

pared very pure bornylene from the methylxanthogenate ester of borneol.

Heating primary or secondary alcohols with mineral acids rarely gives good results except with the simpler members, as in the well-known methods of preparing ethylene and propylene, using sulfuric or phosphoric acids. Wallach showed that concentrated formic acid [157] or oxalic acid [158] give better results in the terpene series than mineral acids. Potassium acid sulfate has been employed with good results, as in the conversion of borneol, which is relatively quite stable, to camphene.[159] When potassium acid sulfate or phosphorus pentoxide is used to dehydrate cyclohexanol-1-acetic acid, cited above, the resulting product is $\Delta^{1,2}$ cyclohexene acetic acid instead of the $\Delta^{1(7)}$ acid which is obtained with acetic anhydride.

Sabatier and Mailhe [160] have shown that phosphorus, carbon, anhydrous calcium sulfate, basic aluminum sulfate and many metallic oxides promote the dehydration of alcohols. The corresponding olefine hydrocarbon is usually produced, although alumina at 210° causes some ether to be formed. Ipatiev found that under higher pressures the formation of ether was considerably increased. Baskerville was unable to detect ether in ethylene resulting from the decomposition of alcohol in contact with thoria at temperatures as low as 250°.[161] Sabatier and Mailhe studied a series of catalysts and, within the temperature range 300°–350°, ethyl alcohol gave varying yields of ethylene and hydrogen, the latter being formed together with acetaldehyde, $CH_3CH_2OH \longrightarrow CH_3CHO + H_2$. Thoria, alumina and blue oxide of tungsten at 340°–350° gave practically quantitative yields of ethylene and the other catalysts gave the results indicated in the following table:

	Per cent ethylene	
ThO_2	100.	
Al_2O_3	98.5	
W_2O_3	98.5	
Cr_2O_3	91.	Dehydration and dehydrogenation
SiO_2	84.	
TiO_2	63.	
BeO	45.	
ZrO_2	45.	
U_3O_8	24.	
Mo_2O_5	23.	
Fe_2O_3	14.	
V_2O_3	9.	
ZnO	5.	

[157] *Ann.* *291,* 361 (1896); *356,* 243 (1907).
[158] *Ann.* *275,* 106 (1893).
[159] Wallach, *Ann.* *230,* 239 (1885).
[160] *Ann. Chim. Phys.* *VIII. 20,* 289 (1910).
[161] *J. Am. Chem. Soc.* *35,* 93 (1913).

SnO	0.	
CdO	0.	
MgO	0.	Dehydrogenation
Cu	0.	
Ni	0.	

Engelder[162] showed that in the presence of Al_2O_3, SiO_2, ZrO_2 and TiO_2 the equilibrium, alcohol $\rightleftarrows$ water $+$ ethylene, could be displaced by the addition of water vapor to the incoming alcohol. Kaolin within the range 350°–400° is particularly efficient in producing ethylene.[163] Ipatiev, prior to the work of Sabatier and Mailhe quoted above, had shown the wide applicability of alumina as a dehydrating catalyst.[164] He prepared isobutylene and pure propylene using alumina as a catalyst and butylene has been made from n.butyl alcohol, on an industrial scale, by the same method.[165] Senderens found that amorphous silica is much more active than ground quartz and aluminum phosphate is also an excellent catalyst; Senderens obtained noteworthy results by decomposing cyclohexanol at 300°, to cyclohexene and menthol to menthene.[166] Pinacone gives excellent yields of dimethylbutadiene when passed over alumina at 450°, but the best yields are obtained *in vacuo*.[167]

The decomposition of tertiary amines has been employed as a laboratory method but the preparation of these amines is comparatively costly and difficult though several processes for the preparation of dienes, leading to the synthesis of rubber, which involve this tertiary amine method, have been patented.[168] As pointed out above, the decomposition of the tertiary amines usually takes place at comparatively low temperatures, thus lessening the probability of decomposition or rearrangement of the resulting olefine. Willstätter and Schmaedel,[169] made cyclobutene in this way.

$$\begin{array}{l} CH_2-CH-NH_2 \\ |\qquad\ | \\ CH_2-CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2-CH-N(CH_3)_3 \\ |\qquad\ |\qquad\ | \\ CH_2-CH_2\quad OH \end{array} \longrightarrow \begin{array}{l} CH_2-CH \\ |\qquad\ \| \\ CH_2-CH \end{array}$$
$$+ N(CH_3)_3 + H_2O$$

The Grignard reaction has sometimes been applied to the synthesis of olefines in ways other than noted above. In rare instances the Grig-

[162] *J. Phys. Chem. 21,* 676 (1917).

[163] The activity of these catalysts is gradually diminished as they become impregnated with carbon, evidently formed by the decomposition of ethylene to methane and carbon.

[164] *Ber. 36,* 1997 (1903); *34,* 596, 3579 (1901).

[165] Newman, *Can. Chem. J. 1920,* 47; King, *J. Chem. Soc. 115,* 1404 (1919).

[166] *Compt. rend. 144,* 1109 (1907); *146,* 125 (1908); Bayer & Co. Brit. Pat. 4,076 (1913).

[167] Badische, French Pat. 417,275 (1910).

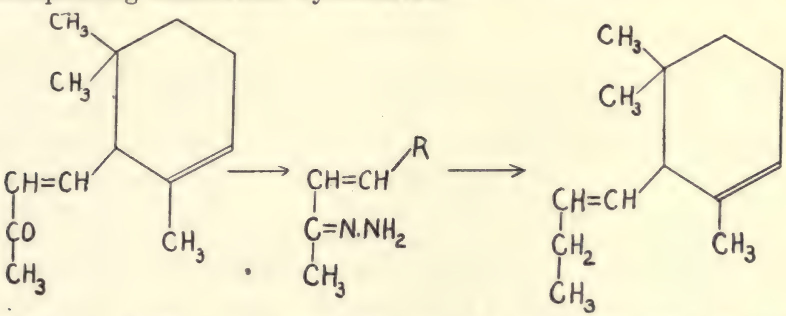
[168] *J. Chem. Soc. 102,* I, 821 (1912).

[169] *Ber. 38,* 1992 (1905).

nard complex $RC\begin{smallmatrix}\diagup OMgX\\ \diagdown R_1\end{smallmatrix}$ breaks down spontaneously, but heat is usually required to effect decomposition to the olefine.[170]

The decomposition of hydrocarbons by heat has not been employed for the preparation of pure olefines, but it is well known that the pyrolytic products of paraffine, petroleum oils and the like are rich in olefines. Pressure, as in distillation of heavy oils under pressure, diminishes the proportion of olefines in the product and decomposition by heat under vacuum increases the proportion of olefines. Dilution of the original hydrocarbon vapors with an inert gas or steam also has this effect.[171]

The reduction of the ketone group to the CH_2 group, in the presence of a cyclopropane ring or unsaturated bonds of the ethylene type and without reducing these double bonds, may, in certain instances, be accomplished by forming the hydrazine derivative of the ketone and then decomposing this by solid caustic potash. Thus carone gives carane, without rupture of the cyclopropane ring, and ionone yields the corresponding unsaturated hydrocarbon.[172]



[170] Harries & Weil, *Ann.* *343*, 363 (1905); Klages, *Ber.* *39*, 2306 (1906); Barbier & Locquin, *Chem. Zentr.* *1913*, II, 28.
[171] Greenstreet, U. S. Pat. 1,110,925.
[172] Kishner, *J. Russ. Phys.-Chem. Soc.* *43*, 1398, 1563 (1911).

Chapter V. Acyclic Unsaturated Hydrocarbons.

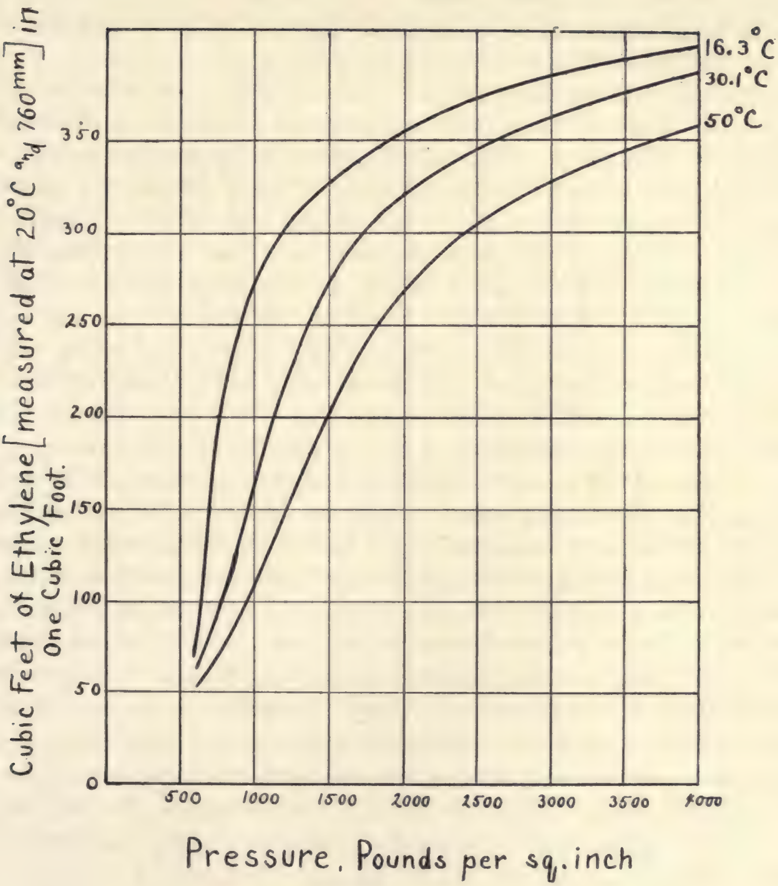
Remarkably few hydrocarbons of this series are known. Many which have been described are undoubtedly mixtures and the constitutions assigned to many of them are undoubtedly incorrect. This is particularly true of olefines of the type $RCH_2CH = CH_2$. The simpler olefines are very reactive and the most promising outlook for the chemical utilization of petroleum is undoubtedly in the direction of these simpler olefines, including the gaseous olefines, ethylene and propylene, and the low boiling highly reactive olefines such as the butylenes, amylenes and hexylenes.

Ethylene

One liter of ethylene under standard conditions weighs 1.2519 grams.[1] Its boiling point at 760 mm. according to Cailletet[2] is — 105° and according to Ladenburg and Krügel[3] is — 105.4°; Burrell and Robertson[4] give — 103.9° as the boiling-point. Its melting-point is — 169°. Its critical temperature is 9.5° ± 0.1, critical pressure 50.65 ± 0.1 atmospheres.[5] Its heat of combustion is stated to be 333,350 and 341,400 calories (Thomsen[6]) and 345,800 calories (Mixter[7]). Data on the compressibility of ethylene and the extent of its deviation from the behavior of a perfect gas under pressure at ordinary atmospheric temperature have recently been published, compressed ethylene, in steel cylinders, for welding and cutting now being commercially available.[8]

Water at 0° dissolves approximately 0.25% ethylene. The gas is markedly soluble in ammoniacal cuprous chloride, but not in am-

[1] Cf. Malisoff & Egloff, *J. Phys. Chem. 23,* 65 (1919).
[2] *Compt. rend. 94,* 1224 (1882).
[3] *Ber. 32,* 1818 (1899).
[4] *J. Am. Chem. Soc. 37,* 1893 (1915).
[5] *J. Chim. Phys. 10,* 504 (1913).
[6] *Thermochem, Unters,* 4, 64.
[7] *Am. J. Sci.* (4), *4,* 51 (1897).
[8] According to British Patents 146,332 and 147,051 (1920), ethylene may be separated from coal gas or oil gas by passing the gas through a series of absorbent materials at low temperatures.



Compressibility of Ethylene.

moniacal silver chloride. Ethylene is also markedly soluble in petroleum oils under moderate pressures; oil gas scrubbed with petroleum oils under pressures of 50 to 150 pounds loses by solution in the oil much more ethylene and propylene than corresponds to the partial pressure of these olefines in the gas mixture. On removing the pressure on the oil solution, gas is liberated which is much richer in olefines than the original.

Ethylene is most easily made by passing ethyl alcohol over kaolin at 350° to 400°. Ethylene was made by this method on a large scale during the late war.[9] When ethyl alcohol is passed over metals at elevated temperatures various amounts of acetaldehyde are formed. Zinc dust at 550° gives a 50% yield of ethylene. Ipatiev [10] used fire clay and alumina with excellent results and Engelder [11] states that with alumina at 350° the resulting gas contains 98.5% ethylene. Sprent [12] gives a slightly higher figure as the best working temperature when using alumina, i. e., 360°. This method of preparing ethylene is intimately connected with the stability of ethylene to heat and the presence of various contact substances. As pointed out by Bone and Coward [13] the importance of the time factor on the character and proportions of the products resulting from the passage of substances through hot tubes has frequently been overlooked. Ethylene is very rapidly decomposed in contact with nickel at 300°, carbon, ethane, methane and hydrogen being formed. This decomposition is much slower, in contact with iron, but is quite rapid above 350°, but according to Ipatiev polymerization occurs in the presence of iron or copper at 400°–450°. In the absence of catalysts such as nickel, no hydrogen is formed from ethane at 450°. According to Day [14] ethylene appears to be very slowly condensed at 350° to 400°, the residual gas containing methane and ethane. According to the early researches of Berthelot, ethylene condenses with benzene to form anthracene when the two hydrocarbons are passed together through a red-hot tube. This reaction has recently been examined by Zanetti and Kandell,[15] who find that the maximum yields of anthracene are obtained at 900° to 925° C.

Numerous attempts have been made to prepare ethylene by partial

[9] Norris, *J. Ind. & Eng. Chem. 11,* 817 (1919).
[10] *Ber. 35,* 1047 (1902); *36,* 1990 (1903).
[11] *J. Phys. Chem. 21,* 676 (1917).
[12] *J. Soc. Chem. Ind. 32,* 171 (1913).
[13] *Rep. Brit. Assoc. 1915,* 368; *Soc. 93,* 1197 (1908).
[14] *Am. Chem. J. 8,* 153 (1886).
[15] *J. Ind. & Eng. Chem. 13,* 208 (1921).

hydrogenation of acetylene, but so far, without commercial success. Karo [16] and others [17] state that 90 to 95% conversion to ethylene can be effected in the presence of active nickel at about 100°. Ethylene, itself, is very rapidly hydrogenated to ethane in the presence of nickel at 150°. The activity of nickel is quickly impaired by the separation of carbon and copper is not very effective, but the change is rapid in the presence of platinum black at 185°, and aqueous *colloidal* platinum or palladinum effect rapid reaction at room temperature.[18] In this, as in many similar reactions in which gas and liquid phases are concerned, the rate of solution of the gas is the chief time controlling factor. During the war this problem was investigated in the laboratory at Edgewood Arsenal, on account of the importance of ethylene in the manufacture of "mustard gas." The process was evidently not carried out on an industrial scale but it was ascertained that in the presence of catalytic nickel prepared by reduction at 300°, both acetylene and ethylene are hydrogenated at temperatures as low as — 10°. No deposition of carbon on the catalyst was noticed when the reaction was carried out at room temperatures. Gas mixtures containing approximately 80% ethylene were obtained, the remaining gas consisting of ethane, nitrogen and a little acetylene.

Ethylene is a minor product in the electrolysis of salts such as acetates, malonates and succinates: it can be made from ethylene bromide by Gladstone's copper-zinc couple, and certain metallic carbides react with water to give small proportions of ethylene (barium carbide and silicide mixture yields a gas containing 15% ethylene). But the only method, other than the hot kaolin method, which is of preparative value, is the old familiar laboratory method of passing alcohol vapor into hot sulfuric or phosphoric acid. In this method of preparation a small proportion of hydrocarbon oil is always noticed in the wash bottles, and this oil is probably a condensation product or polymer of ethylene.[19] Thus zinc chloride at 275° converts ethylene into an oily polymer of specific gravity (15°) 0.751 and anhydrous aluminum chloride effects a similar change at room temperature.

Ethylene may be oxidized without great difficulty to formaldehyde,

[16] Karo, Ger. Pat. 253,160 (1911); Sabatier & Senderens, *Compt. rend.* *128*, 1173 (1899); *130*, 1559, 1628 (1900); *131*, 40, 187 (1900); Paal, *Ber.* *48*, 275 (1915); Paal & Schwarz, *Ber.* *51*, 640 (1918), claim that colloidal palladium gives the best results. A particularly important paper has just appeared by Ross, Culbertson and Parsons, *J. Ind. & Eng. Chem.* *13*, 775 (1921).

[17] Lane, Ryberg & Kinberg, Ger. Pat. 262,541 (1913).

[18] Sabatier & Senderens. *Compt. rend.* *131*, 40 (1900); Paal & Hartman, *Ber.* *42*, 2239 (1909); *48*, 994 (1915).

[19] Montmollin [*Bull. Soc. chim.* (4), *19*, 242 (1916)] has examined this oil mixture and states that it consists chiefly of alkylated naphthenes.

oxalic and acetic acids, glycol, formic acid, etc., but these oxidation products are themselves oxidized more rapidly than ethylene. The major products of the oxidation of ethylene are, therefore, usually CO_2 and water and large yields of intermediate products are not to be expected.

At 400° with insufficient oxygen for complete combustion, a little formaldehyde is formed.[20] With equal volumes of oxygen, carbon monoxide and hydrogen are produced; with less than an equal volume of oxygen Lean and Bone[21] believed two reactions to be involved,

$$C_2H_4 \longrightarrow CH_4 + C$$

$$2C_2H_4 + O_2 \longrightarrow 2CH_4 + 2CO$$

Bone and Wheeler[22] studied the oxidation of ethylene by oxygen at temperatures within the range 250° to 400°, but according to a recent paper by Willstätter[23] the oxidation to formaldehyde is not rapid below 500°. As shown by F. C. Phillips, combustion of ethylene takes place at lower temperatures in the presence of osmium than with other catalytic surfaces and Willstätter finds that in the presence of this metal oxidation of ethylene begins at 130°, carbon dioxide and water being practically the only products. In the presence of copper or silver practically no formaldehyde is produced, and in the case of copper oxidation is fairly rapid at 250°. Willstätter made use of the observation that when ethylene is diluted with an inert gas the thermal decomposition of the ethylene itself is greatly reduced. Metallic surfaces catalyse the thermal decomposition of ethylene and Willstätter accordingly obtained the best yields of formaldehyde by operating without a catalyst at about 585°, using a gas mixture containing 19.38 per cent ethylene and 7.58 per cent oxygen. Under these conditions he obtained approximately 50 per cent of the theory of formaldehyde.

Ozone reacts vigorously with ethylene,[24] an explosive compound being formed. In the presence of water formaldehyde, formic acid, carbon monoxide and hydrogen peroxide are among the reaction products.

Ethylene and oxygen in sunlight at ordinary temperatures do not react but under the influence of ultraviolet light, oxidation to CO_2, CO

[20] Nef, *Ann.* *298*, 202 (1899).
[21] *J. Chem. Soc.* *115*, 144 (1892).
[22] *J. Chem. Soc.* *83*, 1074 (1903).
[23] *Ann.* *422*, 36 (1921).
[24] Harries, *Ann.* *374*, 288 (1910).

and formic acid results.[25] According to Taylor [26] ethylene and oxygen react at ordinary temperatures in the presence of activated charcoal. Chromic acid oxidizes ethylene, with difficulty to CO_2, formic and acetic acids.[27] Potassium permanganate in dilute sulfuric acid yields CO_2, formic and acetic acids, but neutral or alkaline permanganate yields glycol and oxalic acid.[28]

Ethylene combines directly with a large number of substances and while many of these reactions have been known for a great many years, a few of them have become industrially important only within very recent years. Ethylene chlorohydrin was made by Carius [29] and others by treating ethylene with dilute aqueous hypochlorous acid. Gomberg [30] has recently shown that the reaction of ethylene and hypochlorous acid takes place so rapidly that practically quantitative yields of the chlorohydrin are obtained by agitating ethylene with cold chlorine water, although free chlorine is also present. Methods suitable for large scale manufacture of ethylene and propylene chlorohydrins, using chlorine and cold aqueous solutions of sodium carbonate or bicarbonate, have recently been described.[31] Ethylene bromohydrin has recently been made by passing ethylene and bromine vapor separately into ice water, keeping the concentration of the bromine in the solution very low.[32] The bromohydrin had previously been made by the action of HBr on ethylene glycol or by the action of PBr_3 on the glycol. The bromohydrin boils with slight decomposition, at 146°–150° and has a density, 20°, of 1.7629.

Ethylene chlorohydrin reacts with sodium azide, the chlorine being replaced by the triazo group.[33] (Vinyl bromide does not react with sodium azide.) By converting the triazoethyl alcohol to the bromide and replacing the bromine with iodine, the resulting triazoiodine derivative can be decomposed by alkali, removing HI and yielding triazoethylene. The boiling-point of triazoethylene is 26°, or 10° higher than the corresponding bromide $CH_2 = CHBr$.

$$\begin{array}{l} CH_2Cl \\ | \\ CHOH \end{array} + NaN_3 \longrightarrow \begin{array}{l} CH_2N_3 \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CH_2N_3 \\ | \\ CH_2I \end{array} \longrightarrow \begin{array}{l} CHN_3 \\ \| \\ CH_2 \end{array}$$

[25] Berthelot and Gaudechon, *Compt. rend.* *150*, 1327 (1910).
[26] *Trans. Am. Electrochem. Soc.* *1919*, 167.
[27] Chapman & Thorpe, *Ann.* *142*, 182 (1867); Othmar & Feidler, *Ann.* 197, 243 (1879).
[28] *Ann.* *150*, 373 (1869); *Ber.* *21*, 1234 (1888). Cf. Evans on oxidation of ethylene glycol by permanganate, *J. Am. Chem. Soc.* *41*, 1385 (1919).
[29] *Ann.* *126*, 197 (1863); Butlerow, *Ann.* *144*, 40 (1867).
[30] *J. Am. Chem. Soc.* *41*, 1414 (1919).
[31] Brooks, *Chem. & Met. Eng.* *22*, 629 (1920).
[32] Read & Hook, *J. Chem. Soc.* *117*, 1214 (1920).
[33] Forster & Newman, *J. Chem. Soc.* *97*, 2570 (1910).

Ethylene chlorohydrin gave promise of becoming of some importance during the recent war, as an intermediate in the manufacture of dichloroethyl sulfide (mustard gas), but another reaction of ethylene, i. e., its reaction with sulfur chloride, first discovered by Guthrie,[34] proved to be more suited to large scale production and was adopted in all the Allied countries. The experimental conditions, of which Guthrie's work gave little more than a hint, were worked out by Pope[35] and the large scale operations worked out by Levinstein. Gibson and Pope[36] showed that when the reaction between ethylene and sulfur chloride is carried out above 70° considerable decomposition occurs and Pope and his assistants showed in a later paper[37] that practically quantitative yields are obtained when the ethylene contains a little alcohol vapor but when pure ethylene is employed the product is not so pure, thus explaining the discrepancies reported by other workers. The sulfur liberated in the reaction appears to be retained largely in a colloidal condition and may be separated by dissolving the dichloro sulfide in kerosene and then separating the mustard gas from the kerosene solution by chilling. Distillation in vacuo readily yields pure ββ-dichloroethyl sulfide. In Germany the chlorohydrin method of making mustard gas was employed.

Ethylene reacts with selenium monochloride[38] to give free selenium and the product $Cl_2Se(CH_2CH_2Cl)_2$.

The reactions of the two manufacturing processes for mustard gas are as follows:

(1)
$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + HOCl \longrightarrow \begin{array}{l} CH_2-OH \\ | \\ CH_2-Cl \end{array}$$

$$2\begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + Na_2S \longrightarrow \begin{array}{lcl} CH_2OH & & CH_2OH \\ | & & | \\ CH_2 & -S- & CH_2 \end{array}$$

$$\begin{array}{lcl} CH_2OH & & CH_2OH \\ | & & | \\ CH_2 & -\!\!-\!\!-S-\!\!-\!\!- & CH_2 \end{array} + 2HCl \longrightarrow \begin{array}{lcl} CH_2Cl & & CH_2Cl \\ | & & | \\ CH_2 & -S- & CH_2 \end{array}$$

(2)
$$2\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + S_2Cl_2 \longrightarrow \begin{array}{lcl} CH_2Cl & & CH_2Cl \\ | & & | \\ CH_2 & -\!\!-\!\!-S_2-\!\!-\!\!- & CH_2 \end{array} \longrightarrow$$

[34] *Ann.* *119*, 91 (1861) ; *121*, 108 (1862).

[35] *J. Soc. Chem. Ind.* *38*, 344R, 434R (1919) ; Green, *J. Soc. Chem. Ind.* *38*, 363R, 469R (1919).

[36] *J. Chem. Soc.* *117*, 271 (1920).

[37] *J. Chem. Soc.* *119*, 634 (1921).

[38] Bausor, Gibson & Pope, *J. Chem. Soc.* *117*, 1453 (1920) ; Heath & Semon, *J. Ind. & Eng. Chem.* *12*, 1100 (1920).

$$\begin{array}{ccc} CH_2Cl & & CH_2Cl \\ | & & | \\ CH_2 & -\!\!-\!\!-\, S \,-\!\!-\!\!- & CH_2 \end{array} + S$$

Phosgene reacts with ethylene under the influence of light as follows.[39]

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + COCl_2 \longrightarrow \begin{array}{l} CH_2Cl \\ | \\ CH_2COCl \end{array} \text{ (Chloropropionyl chloride).}$$

Norris and Couch [40] have shown that benzoyl chloride reacts with ethylene in the presence of anhydrous aluminum chloride to give phenyl vinyl ketone, a reaction probably capable of considerably wider application. Ethylene is readily absorbed by anhydrous aluminum chloride and benzene to form mono- and poly-substituted ethyl benzenes.[41]

Chlorine and bromine [42] react smoothly with ethylene to give the symmetrical dihalides. The addition of chlorine to ethylene to form ethylene chloride or "Dutch liquid" was first carried out in 1796 and Faraday later treated oil gas [43] with chlorine obtaining ethylene chloride together with other chlorinated products. Although this reaction has been known since this early date, no very thorough study of it has been made. Dry chlorine and ethylene react exceedingly slowly. Ethylene passed into chlorine water yields ethylene chlorohydrin almost exclusively; cold dilute bromine water yields both ethylene bromide and ethylene bromohydrin. In chlorinating ethylene, it is difficult to limit the chlorination to the dichloride, trichloroethane and still more highly chlorinated products being formed. The introduction of ethylene into liquid chlorine in the cold, under pressure, gives excellent yields of ethylene chloride,[44] and chlorination in the presence of charcoal, alumina or other very porous material is stated to give good yields.[45] Another patentee employs solid calcium chloride as a catalyst.[46] Higher olefines, amylenes and hexylenes, yield dichlorides when treated with sulfuryl chloride below 30°.[47] When chlorine is absorbed in cold bromine in the proportions required by the hypothetical sub-

[39] Lippman, *Ann.* **129,** 81 (1864).
[40] *J. Am. Chem. Soc.* **42,** 2330 (1920).
[41] Balsohn, *Bull. Soc. chim.* (2), **31,** 529 (1879).
[42] According to Plotnikov, *Chem. Abs.* 1917, 48, ethylene and bromine react even at — 80° in the dark.
[43] The oil gas used by Faraday was probably made from fatty oils, which, however, closely resembles oil gas made from mineral oils in its general character.
[44] Curme, U. S. Pat. 1,315,545; 1,315,547.
[45] Harding, Brit. Pat. 126,511 (1918).
[46] Smythe, *Gas. J.* **149,** 691 (1920). A yield of 50% ethylene chloride by this method is reported.
[47] Badische Co., *J. Soc. Chem. Ind.* **1912,** 151.

stance BrCl and ethylene is then introduced, the principal product is $CH_2Cl.CH_2Br$, which appears to be the only real evidence of the existence of the compound Cl.Br.[48] Bromine has practically no action on ethylene bromide. Iodine reacts slowly with ethylene in direct sunlight or on heating to 60°.[49]

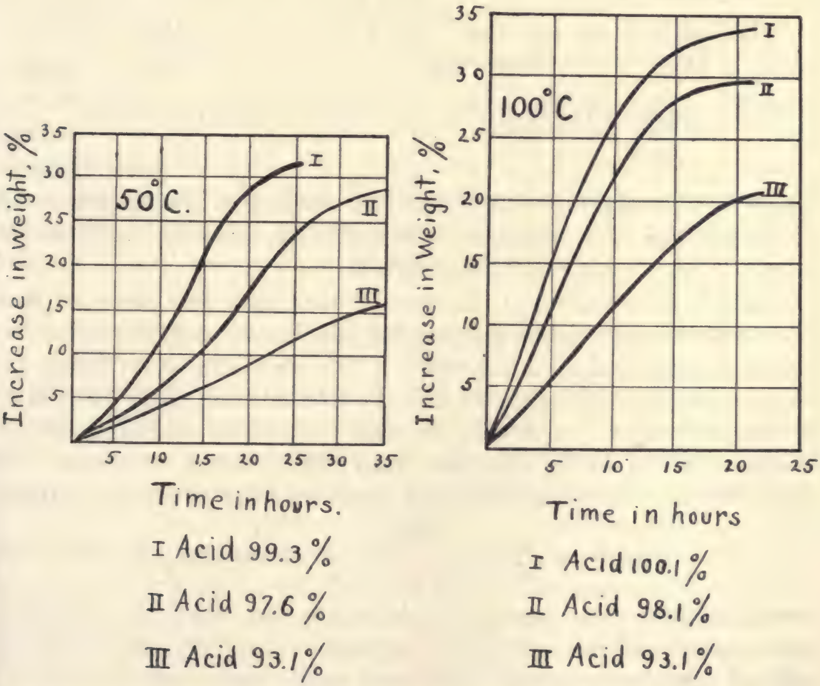
Iodine monochloride and ethylene yields ethylene chloride and free iodine. Concentrated hydriodic and hydrobromic acids combine slowly with ethylene at 100°.

Boron trifluoride reacts with ethylene forming the product $C_2H_3BF_2$ boiling at 125°.[50]

The reaction of sulfuric acid and the simpler gaseous olefines has recently become a matter of industrial interest since the alkyl sulfates may be saponified or hydrolyzed by steam to the corresponding alcohols. As first described by Faraday [51] in 1827, the absorption of ethylene by concentrated sulfuric acid, with the formation of ethyl hydrogen sulfate, is not rapid below 160° and according to Butlerow [52] the absorption is rapid at 160°–170°. The question of an industrial synthesis of alcohol from gases containing ethylene was investigated in 1855 by Berthelot [53] and later by P. Fritzsche [54] who states that 100 kilos of concentrated acid are required to produce 18 kilos of alcohol. The chief difficulties have been the handling and re-concentration of relatively large quantities of sulfuric acid and loss of acid by oxidation and charring of other olefines, which were not completely removed prior to the absorption of ethylene. One patentee claims that vanadium or uranium salts facilitate the absorption of ethylene.[55] Ferrous sulfate and cuprous salts are said to promote the absorption of ethylene and under these conditions [56] the gas is treated with acid at 100°–120°. Very recently, Bury and Ollander [57] have carried out these reactions on an industrial scale, in England, and state that one ton of Durham coal yields sufficient ethylene to produce 1.6 gallons of 95 per cent ethyl alcohol. After removing benzene vapors and olefines other than ethylene, the gas is scrubbed by hot 95 per cent sulfuric acid and the resulting ethyl-hydrogen sulfate is hydrolyzed by steam. Since

[48] Delépine & Ville, *Bull. Soc. chim.* *27*, 673 (1920).
[49] Faraday, *Phil. Trans.* *18*, 118; Regnault, *Ann. d. Chimie.* (2), *59* (1835).
[50] Landolt, *Ber.* *12*, 1586 (1879).
[51] *Pogg, Ann.* *9*, 21 (1827).
[52] *Ber.* *6*, 196 (1873).
[53] *Compt. rend.* *40*, 102 (1855); *Ann. Chim.* (3), *43*, 385 (1855).
[54] *Chem. Ind.* *20*, 266 (1897); *35*, 637 (1912).
[55] Lattre, French Pat. 468,244; *J. Soc. Chem. Ind.* *1914*, 953; Loisy, *Compt. rend.* *170*, 50 (1920).
[56] Brit. Pat. 152,495, *J. Soc. Chem. Ind.* *39*, 833A (1920).
[57] Brit. Pat. 147,360 (1914); *Chem. Weekblad.* *17*, 478 (1920).

coal gas ordinarily contains not over 2.5 per cent ethylene, it would be reasonable to assume that such a process would be more successful with oil gas or waste gas from petroleum stills, particularly cracking or coking stills, gas from the latter source containing 5 to 6 per cent ethylene. Propylene and butylenes are absorbed by sulfuric acid at ordinary temperatures and according to Hunt [58] and Ellis [59] good yields of isopropyl and secondary butyl alcohols are obtainable in this way. By the Ellis process isopropyl alcohol is obtained from propylene contained in the gases from Burton stills used in cracking petroleum oils to make gasoline. The gases are allowed to bubble through cool sulfuric acid of specific gravity 1.8 until the gravity falls to 1.3 or 1.4.



Absorption of Ethylene in Sulfuric Acid of Different Concentrations, at 50° and 100° C

The acid liquor is diluted with water and polymers, higher alcohols, etc., allowed to separate. The diluted liquid is distilled with steam. A small amount of olefines and propyl ether first appear in the distillate.

[58] Brit. Pat. 146,956; 146,957 (1920).
[59] *Oil, Paint & Drug Rep.* Dec. 20, 1920, p. 28.

Isopropyl alcohol then comes over. The rate of absorption of ethylene, in a small experimental apparatus, at 50° and 100°, is shown in the accompanying figures. These values are entirely empirical but give a good comparison of the absorption in acids of different concentration.[60]

The reaction of ethylene with mercury salts is well known through the work of Hoffman and Sand.[61] They conclude that the following types of salts are formed, to which they have given the names indicated,

(1) Ethene mercury salts, $CH_2CH.HgX$

(2) Ethanol mercury salts, $\begin{array}{l} CH_2OH \\ | \\ CH_2HgX \end{array}$

(3) Ethyl ether mercury salts, $XHgC_2H_4OC_2H_4HgX$

(4) Polymerized ethene mercury salts $(C_2H_3HgX)_n$

They proposed the theory of the initial formation of $\begin{array}{l} CH_2X \\ | \\ CH_2HgX, \end{array}$ which by decomposing with loss of HX would give ethene compounds, or by reacting with water ethanol salts. Hydrochloric acid decomposes all four types, liberating ethylene.

Sand[62] later expressed the opinion that only two series of compounds are formed and stated that the fourth class, polymerized ethene mercury compounds, did not exist. Later writers have confirmed this view.[63] Manchot[64] has shown that the ethanol compound C_2H_5OHgCl is monomolecular. In view of the ease with which cold dilute hydrochloric acid liberates *ethylene* from this ethanol compound, not CH_3CH_2OH, as the Sand structure would lead one to expect, Manchot favors the structure $C_2H_4Hg{<}\begin{array}{l} OH \\ Cl, \end{array}$ the ethylene group being held in combination in some manner analogous to the way CO is combined with cuprous chloride. Manchot explains the stability of the mercury ethanol compound towards nitric and acetic acids and its reactivity to hydrochloric acid by the theory that mercuric chloride is capable of forming the double compound, $HgCl_2.2HCl$. The equations for its decomposition by HCl would then be expressed as follows:

[60] Plant and Sidgwick, *J. Soc. Chem. Ind. 1921*, 14T.
[61] *Ber. 33*, 1340, 2692 (1900); *34*, 1385 (1901).
[62] *Ber. 34*, 1385 (1901).
[63] Manchot, *Ann. 430*, 174 (1920).
[64] Loc. cit.

$$(1)\qquad C_2H_4Hg{<}\begin{matrix}OH\\Cl\end{matrix} + HCl \leftrightarrows C_2H_4HgCl_2 + H_2O$$

$$(2)\qquad C_2H_4HgCl_2 + 2HCl \leftrightarrows HgCl_2, 2HCl + C_2H_4$$

The constitution of these compounds can hardly be regarded as definitely determined.

Curme [65] has described a method of separating ethylene in a pure condition from gas mixtures, which consists in absorbing the ethylene in a solution containing a mercury salt, such as mercuric sulfate, and subsequently heating the solution to expel the ethylene.

With mercuric acetate in methyl alcohol the ether $\begin{matrix}CH_2HgOAc\\|\\CH_2OCH_3\end{matrix}$ is formed.[66] Manchot and Brand [67] state that ethylene forms a double compound with cuprous chloride. A double compound with platinum chloride, $C_2H_4PtCl_2$, is known,[68] and concentrated aqueous ferrous bromide forms the crystalline compound $C_2H_4FeBr_2.2H_2O$. Henderson and Gangloff [69] isolated double compounds with anhydrous aluminum chloride (from absolute alcohol) having the formulæ $AlCl_3.C_2H_4.2C_2H_5OH$ and $AlCl_3.C_2H_4.CH_3OH.H_2O$.

Propylene and Substituted Propylenes

The best laboratory method for the preparation of propylene is the decomposition of isopropyl alcohol by passing over aluminum phosphate or kaolin at about 300°.[70] It is liquid under 7 to 8 atmospheres pressure and would probably be industrially valuable in this form. Propylene forms propanol mercury salts analogous to those of ethylene; Curme [71] describes the use of ethanol salts to separate pure ethylene from inert gaseous diluents but the similar treatment of gaseous mixtures containing propylene has not been described. The source of propylene utilized by Ellis for the preparation of isopropyl alcohol by means of the sulfuric acid esters, is oil gas or petroleum still gas. Propylene may be separated from ethylene almost quantitatively by means of sulfuric acid (see above).

[65] U. S. Pat. 1,315,541 (1919).
[66] Schoeller, Schrauth & Essers, *Ber. 46*, 2864 (1913).
[67] *Ann. 370*, 286 (1909).
[68] Birnbaum, *Ann. 195*, 69 (1868); Zeise, *Pogg. Ann. 21*, 497,592; *40*, 234 (1837).
[69] *J. Am. Chem. Soc. 38*, 1382 (1916).
[70] Senderens, *Compt. rend. 144*, 1110 (1907). The necessary isopropyl alcohol may be prepared by the reduction of acetone by sodium.
[71] U. S. Pat. 1,315,541.

The chemical properties of propylene are of interest as showing the marked difference in chemical behavior, as compared with ethylene, due to the introduction of a methyl group in ethylene. Whereas ethylene passed through 98.1% sulfuric acid at 70° gives an increase in weight in 2.5 hours, of only 2.27 per cent, propylene at a much lower temperature, 25°, in the same apparatus and using 97% sulfuric acid, showed a gain in weight of 50 per cent in two hours.[72] Propylene reacts with hypochlorous acid, to form the two chlorohydrines, more rapidly than ethylene, and in contrast with ethylene is absorbed by concentrated hydriodic acid in the cold;[73] it is also absorbed, though less rapidly, by concentrated hydrochloric and hydrobomic acid.

The derivatives of propylene have been the despair of those who have sought to formulate simple rules for the addition of other substances to the olefine group. Usually these rules have been based upon ideas of electrical polarity and an arrangement of the additive substance which would supposedly satisfy best the balance of the forces of attraction and repulsion. A few examples will suffice to show the difficulty of forming generalizations which will hold true in this simple series. In reactions where two substances are formed the * indicates the principal product.[74]

$$CH_3CH = CHCl + HBr \longrightarrow \begin{cases} CH_3CH_2CHBr.Cl \; * \\ CH_3CHBr.CH_2Cl \end{cases}$$

$$CH_3CCl = CH_2 + HI \longrightarrow CH_3CClI.CH_3$$

$$CH_3CCl = CH_2 + HBr \longrightarrow CH_3CCl.Br.CH_3$$

$$CH_2Cl - CH = CH_2 + HBr \longrightarrow \begin{cases} CH_2Cl.CH_2CH_2Br \; * \\ CH_2Cl.CHBr.CH_3 \end{cases}$$

$$CH_3CH = CHCl + Cl_2 \xrightarrow{\text{dark}} CH_2Cl.CH = CHCl$$

$$CH_3CH = CHCl + Cl_2 \xrightarrow{\text{light}} CH_3CHCl.CHCl_2$$

$$CH_3CCl = CH_2 + Cl_2 \xrightarrow{\text{dark}} CH_2Cl.CCl. = CH_2$$

$$CH_2Cl.CCl = CH_2 + HCl \longrightarrow CH_2Cl.CCl_2CH_3$$

$$CH_3CH = CHBr + HBr \longrightarrow \begin{cases} CH_3CHBr.CH_2Br \; * \\ CH_3CH_2CHBr_2 \end{cases}$$

$$CH_3C.Br = CH_2 + HBr \longrightarrow CH_3CBr_2CH_3$$

$$CH_2BrCH = CH_2 + HBr \longrightarrow \begin{cases} CH_2Br.CHBr.CH_3 \\ CH_2Br.CH_2CH_2Br \end{cases}$$

[72] Plant & Sidgwick, *J. Soc. Chem. Ind.* *40*, 17 T. (1921).
[73] Butlerow, *Ann.* *145*, 275 (1868); Michael, *J. prakt. Chem.* (2), *60*, 445 (1899).
[74] Reboul, *Ann. Chim.* (5) *14*, 461 (1878); Michael, *Ber.* *39*, 2787 (1906).

ββ'-dichloro-n-propyl sulfide, analogous to mustard gas, has been described by Coffey,[75] who obtained it easily from propylene chlorohydrin by means of Clarke's[76] modification of Victor Meyer's method.[77] Coffey was unable to make the dichloro sulfide from sulfur chloride and propylene although in the case of ethylene the results leave little to be desired. With propylene, condensation to dark colored semi-solid material results, when the reaction is carried out at 50° to 60°.

The Butylenes and Amylenes: There are three butylenes, i. e., $CH_3CH_2CH = CH_2$, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH_2$ and $CH_3CH = CHCH_3$, the latter hydrocarbon being known in *cis* and *trans* form,[78]

$$\begin{matrix} HC.CH_3 \\ \| \\ HC.CH_3 \end{matrix} \qquad\qquad \begin{matrix} HC.CH_3 \\ \| \\ CH_3C.H \end{matrix}$$

cis, boiling-point 1 to 1.5° *trans,* boiling-point 2.5°

When primary or secondary butyl alcohol or the corresponding halides are decomposed, all three butylenes are formed.[79] The difficulty of preparing pure olefines has repeatedly been emphasized in these pages. The butylenes occur in oil gas, in the light liquid, condensed under pressure, from Pintsch-gas, and in the fore runnings of the distillation of crude benzene, particularly when made by low temperature carbonization of coal or from water gas tar. The butylenes are not at present utilized industrially. Their physical properties are very imperfectly known but their boiling points, as recorded, are as follows,

Butene–(1),	boiling-point	—5°
Butene–(2),	" "	cis + 1 to 1.5°; trans + 2.5°.
Isobutylene,	" "	—6°.

Isobutylene can readily be prepared by dropping tertiary butyl iodide into boiling water, the hydriodic acid being retained by the water.[81]

[75] *J. Chem. Soc. 119,* 94 (1921).
[76] *J. Chem. Soc. 101,* 1583 (1912).
[77] The writer experimented with this method, in cooperation with the U. S. Chemical War Service in 1917 and 1918, in the effort to utilize the ethylene and propylene in oil gas. The yields of the dichloro sulfide are good, in the case of propylene, but the product is much less toxic than the ethylene derivative.
[78] Wislicenus, *Ann. 313,* 228 (1900).
[79] Faworski, *J. prakt. chem.* (2), *42,* 153 (1890); Senderens, Compt. rend. 144, 1110 (1907); Newman, *Can. Chem. J. 1920,* 47 and, King, *J. Chem. Soc. 1919,* 1404, describe the catalytic decomposition of n.butyl alcohol to butylene, which is then treated with 80% sulfuric acid to obtain *secondary* butyl alcohol, which in turn may be catalytically dehydrogenated to obtain methyl ethyl ketone.
[80] Wislicenus, *loc cit.*
[81] Nef, *Ann. 318,* 23 (1901); Cf. Ipatiev, *Ber. 40,* 1829 (1907).

Isobutylene is rapidly dissolved by 70 per cent sulfuric acid in the cold; when such a solution made up with 50 per cent acid is warmed to 100° di-isobutylene C_8H_{16} is formed, and when acid of stronger concentration, 80 per cent, is employed tri-isobutylene is formed, illustrating a very general behavior of olefines, i. e., that the more concentrated the acid the further the polymerization proceeds.[82]

The butylenes form characteristic crystalline nitrosates, or rather *bis*-nitrosates, when nitrogen peroxide is passed into cold ether solutions;[83] reduction of these nitrosates yields the corresponding diamines. Isobutylene reacts with acetyl chloride in the presence of zinc chloride to form a chloroketone.[84]

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH_2 + CH_3COCl \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CCl.CH_2COCH_3$$

which decomposes on heating to mesityl oxide. The above reaction is analogous to the reaction between ethylene and benzoyl chloride in the presence of anhydrous aluminum chloride, discovered by Norris and Couch.[85] As noted in connection with the action of sulfuric acid on olefines, the butylenes and amylenes are much more reactive than their higher homologues, and it is therefore probable that in the presence of aluminum chloride the rate of polymerization may greatly exceed that of condensation with other substances as in Norris's reaction. Very probably the higher olefines such as the decylenes will give better yields of condensation products, in the presence of aluminum chloride, than butylene or amylenes.

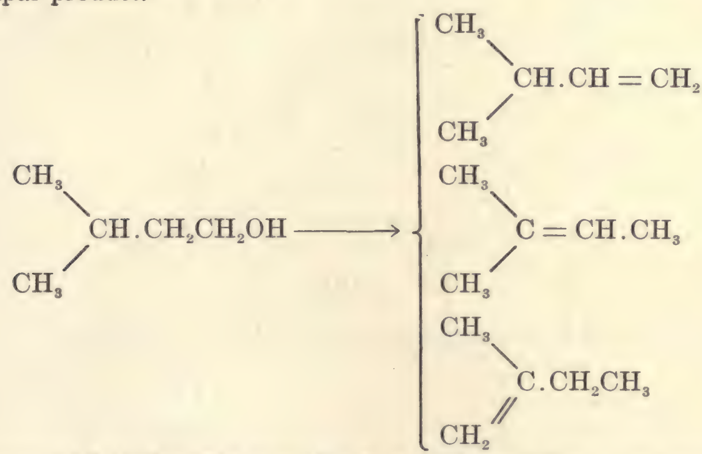
The *amylenes* have probably been more thoroughly studied than any of the olefines with the exception of certain of the terpenes. This is perhaps to be explained by the availability of the raw materials, amyl alcohol and petroleum pentane. Of the five possible amylenes, four are definitely known but pentene-(1) certainly never has been prepared in a pure state and it is doubtful if the material supposedly isolated by Brochet,[86] from the distillate of bog head coal, contained any of this hydrocarbon at all. It is also doubtful if pentene-(2) has

[82] Butlerow, *Ann.* *180,* 247 (1876); *189,* 48 (1877); *Ber.* *12,* 1482 (1879); Brooks & Humphrey, *J. Am. Chem. Soc.* *40,* 822 (1918).
[83] Ssiderenko, *Chem. Zentr.* *1907,* I, 399.
[84] Kondakow, *J. Russ. Phys.-Chem. Soc.* *26,* 12 (1894).
[85] *J. Am. Chem. Soc.* *42,* 2329 (1920).
[86] *Bull. chim. & Phys.* (3), *7,* 567 (1892); Wurtz, *Ann.* *148,* 136 (1868), and Wagner & Saizew, *Ann.* 179, 304 (1875), attempted to prepare this hydrocarbon by the reaction of allyliodide and zinc ethyl; reaction of magnesium ethyl bromide and allyl bromide should yield this hydrocarbon in a pure state, analogous to the preparation of hexene-(1) by Brooks and Humphrey, *J. Am. Chem. Soc.* *40,* 822 (1918). When this hydrocarbon is prepared its boiling point, by analogy from the hexenes, will probably be found to be below 35° instead of 39°-40° as given by Brochet.

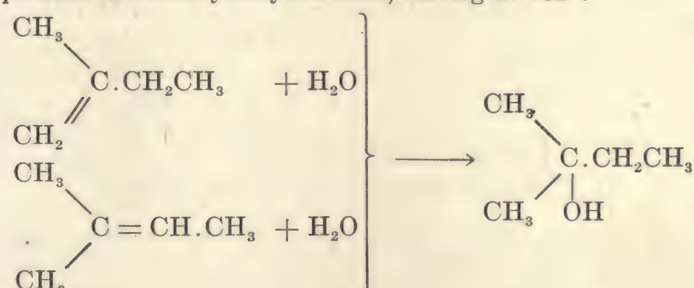
been prepared in a fairly pure condition. It is idle therefore to compare the physical properties of these isomeric amylenes. The most stable of the amylenes is trimethylethylene and it is formed when any of the other amylenes are prepared at high temperatures. According to Ipatiev[87] 2-methylbutene-(3), is almost quantitatively converted into trimethylethylene by passing over heated alumina,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CH.CH=CH_2 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_3$$

When ordinary amyl alcohol is passed over alumina at 340°–350° all three of the methylbutenes are formed, trimethylethylene being the principal product.[88]



Commercial "amylene" is accordingly a mixture of these hydrocarbons containing trimethylethylene as the principal constituent. When such amylene is treated with 70 per cent sulfuric acid in the cold, the principal product is dimethylethylcarbinol, boiling at 102°.



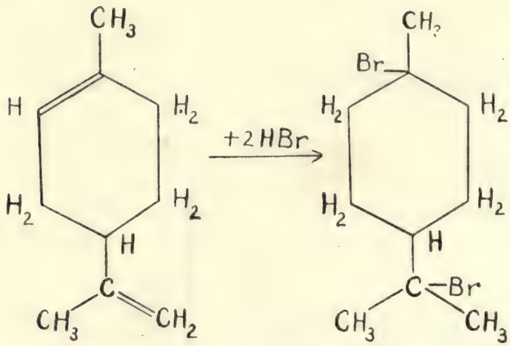
[87] *Ber.* *36*, 2004 (1903).
[88] Senderens, *Compt. rend.* *171*, 916 (1920).

Sulfuric acid in methyl alcohol and trimethylethylene gives the methyl ether.[89]

It is worthy of note, that most of the reactions of the amylenes are applicable to the terpenes, and vice versa. The chemical behavior of the two groups of hydrocarbons is entirely similar, but the use of the word "hydro-aromatic" for the cyclohexane derivatives has probably done a great deal to prevent the full realization of the similarity, one might say *homogeneity,* of the chemistry of the non-benzenoid hydrocarbons. For the purpose of emphasizing this similarity a number of reactions of amylenes and terpenes will be noted.

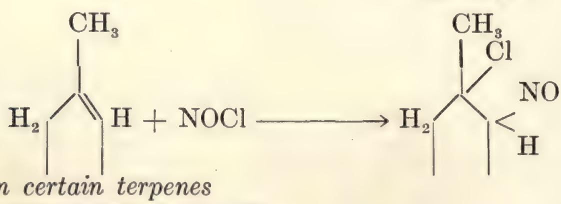
(1) Addition of HCl and HBr (in acetic acid solution).

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH.CH_3 \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\underset{\displaystyle Br}{\underset{|}{C}}.CH_2CH_3$$



(2) Addition of nitrosyl chloride.[90] [91]

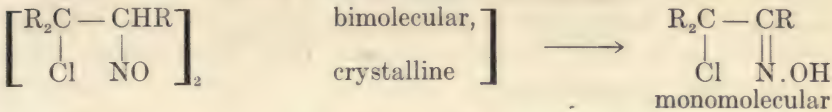
$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CH.CH_3+NOCl\longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\underset{\displaystyle Cl}{\underset{|}{C}}-\underset{\displaystyle NO}{\underset{|}{CH}}.CH_3$$



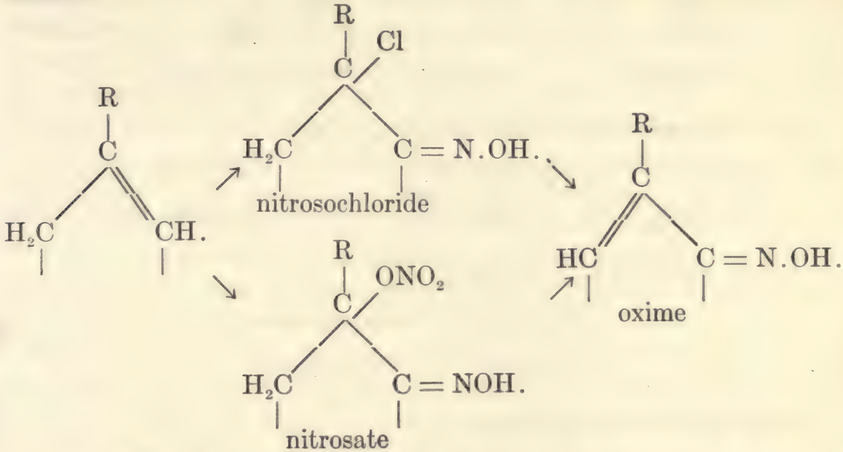
[89] Reychler, *Chem. Zentr.* *1907,* I, 1125.
[90] J. Schmidt, *Ber.* *35,* 3732 (1902) ; *36,* 1765 (1903).
[91] Wallach, *Ann.* *245,* 245 (1888) ; *Ber.* *24,* 1535 (1891).

(3) Behavior of nitroso chlorides.[92]

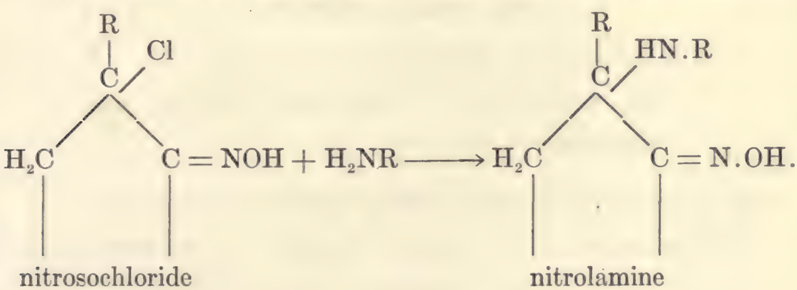
Both amylenes and terpenes,



(4) Behavior of nitrosochlorides and nitrosates; formation of oximes.[93]



(5) Behavior of nitroso chlorides: formation of nitrolamines.[94]



(6) Addition of N_2O_4

amylenes ⟶ bimolecular or bis-nitrosates

terpenes ⟶ " " "

[92] Baeyer, *Ber.* *28*, 1586 (1895); *Ber.* *29*, 1078 (1896).

[93] Best carried out by heating with sodium acetate in acetic acid. Wallach, *Ann.* *374*, 202; *379*, 135.

[94] Wallach, *Ann.* *241*, 296 (1887); *262*, 327 (1891); *Ann.* *245*, 253 (1888); *345*, 143 (1906).

(7) Oxidation, parallel behavior, e. g., $KMnO_4$

trimethylethylene ⟶ glycol.

terpenes ⟶ glycols.

(8) Dilute sulfuric acid,

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\displaystyle OH}{\underset{|}{C}}.CH_2CH_3$$

terpenes ⟶ terpene alcohols

(9) Concentrated mineral acids,

amylenes ⟶ diamylenes ⟶ triamylenes, etc.

terpenes ⟶ diterpenes ⟶ trimerides, etc.

(10) Action of zinc chloride,

amylenes ⟶ polymers

terpenes ⟶ polymers

(11) Behavior on heating,

amylenes, rearrangement to more stable form chiefly trimethylethylene,

terpenes, rearrangement to more stable forms,

e. g., pinenes ⟶ dipentene, terpinene

phellandrenes ⟶ " "

(12) Halides, heated with sodium acetate in acetic acid,

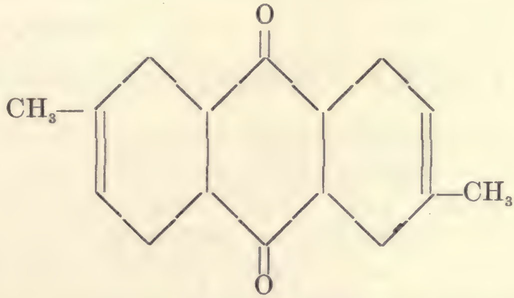
chloropentanes ⟶ amyl acetate + amylenes

$$\text{bornyl chloride} \longrightarrow \text{bornyl acetate} + \left\{ \begin{matrix} \text{Camphene} \\ \text{Bornylene} \end{matrix} \right.$$

Also, the behavior of the amylenes and the terpenes to bromine, ozone, catalytic hydrogenation, air oxidation, and many other reactions, is very closely parallel.

Pentadienes: The preparation and polymerization of isoprene, piperylene and dimethylallene have been discussed in the chapter on polymerization and the problem of synthetic rubber. *Piperylene,*

$CH_3.CH = CH.CH = CH_2$, may be identified by its physical properties (noted in the table on page 231) and by its tetrabromide, 1.2.3.4-tetrabromopentane, known in two stereo-isomeric forms (1) crystalline form, melting point 114.5° and (2) a liquid, distilling at 115°–118° (4 mm.).[95] Oxidation of piperylene by permanganate yields formic and acetic acid. Harries[96] endeavored to prove its constitution by means of its reaction with ozone but without success; it combines only slowly with ozone but the diozonide was so explosive that no definite results were obtained. Auwers[97] concludes from the exaltation of its refractive index that the double bonds are in the conjugated position. The isomer *1.4-pentadiene*, $CH_2 = CH.CH_2CH = CH_2$, is one of the products of the decomposition of pentamethylenediamine nitrite but it has only been isolated in the form of its tetrabromide,[98] melting-point 86°–87°. The preparation and polymerization of *isoprene* is also discussed in connection with the subject of synthetic rubber. Isoprene in glacial acetic acid solution combines with two molecules of hydrogen bromide to form $CH_2Br.CH_2CBr(CH_3)_2$, and with hypochlorous acid to form a dichlorohydrin melting at 82°. It condenses with benzoquinone when the two are heated together at 120°–180°, the product melting at 234°, and since it yields a dioxime and a tetrabromide Euler and Josephson[99] conclude that the combination has occurred through the double bonds in the isoprene, and the quinone, the product probably having the following constitution.



According to Ostromuislenski isoprene may be estimated when present in a mixture of butylenes, amylenes, benzene, etc., by shaking with about ten volumes of fuming hydrochloric acid for six hours; the prod-

[95] Magnanini, *Gazz. Chim. Ital. 16*, 391.
[96] *Ann. 410*, 1 (1915).
[97] *Ber. 49*, 827 (1916).
[98] Demjanow, *Ber. 40*, 2590 (1907).
[99] *Ber. 53*, 822 (1920).

uct is washed with cold brine, dried over calcium chloride and distilled. The fraction distilling at 50°–90° contains butyl and amyl chlorides, the fraction from 90°–130° is separately collected and then, the temperature rising rapidly from 130° to 142°, the 2.4-chloro-2-methylbutane fraction in a fairly pure condition is collected at this temperature. Refractionation of the fraction boiling at 90°–130° will yield a further small proportion of the dichloride.

Olefines, Six to Nine Carbon Atoms: Very few of the many possible hexenes, heptenes, octenes and nonenes have ever been prepared, but their properties may be roughly assumed from the behavior of the impure mixtures, which have been prepared and from the properties of olefines of the terpene class, many of which have been carefully investigated. Certain hydrocarbons of this series are incorrectly described in the literature, for example, hexene-(1) boils at 62°–63°, and the hydrocarbon described by Brochet [100] boiling at 67° which he separated from a distillate from bog head coal, is probably a mixture containing chiefly hexene-(2), (see pp. 151-152). High temperatures, and many chemical reagents, particularly acids, cause such α-olefines to rearrange or the double bond to shift its position. Only reactions employing low temperatures and absence of isomerizing reagents can be expected to produce these α-olefines in any degree of purity, for example,

$$Mg<\begin{matrix}CH_2CH_2CH_3\\ Br\end{matrix} + BrCH_2CH{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2CH{=}CH_2 + MgBr_2$$

or von Braun's method of decomposing trialkyl ammonium hydroxide.[101]

The hexene obtained by treating secondary hexyl iodide (from mannite and HI with alcoholic caustic potash is a mixture of hexene-(1) and hexene-(2). Tetramethylethylene $(CH_3)_2C=C(CH_3)_2$, is the best known of the hexenes and is probably the most stable. Of the heptenes only three are known in fairly pure state, and only two of the many possible nonenes are definitely known. These hydrocarbons have been relatively of such little importance that they will not be described in detail. Most of them, as described, are obviously impure and so few of the many possible hydrocarbons are known that it is impossible to learn anything from a study of their physical properties.

[100] *Bull. Chim. & Phys.* (3) 7, 568 (1892).
[101] *Ann.* 382, 22 (1911).

As regards their chemical properties, it should be kept in mind that in the majority of cases one is dealing with mixtures. Nearly all of the olefines of this series combine with hydroiodic acid in the cold, form nitrosochlorides and nitrosates (which have been definitely described in but a few cases), and behave normally toward most of the reagents affecting olefines. Sulfuric acid yields varying proportions of polymers, alcohols and alkyl sulfuric esters.

None of the known chemical reactions of these olefines offer much promise that the unsaturated hydrocarbons in unrefined gasoline will be utilized. They can be removed practically unchanged by extraction with liquid sulfur dioxide and their conversion to alcohols, ketones and acids would not be matters of great difficulty. Such products, if made, would be mixtures and, therefore, entirely unsuitable for certain uses, for example, perfumes, flavoring materials and pharmaceuticals.

When one reviews the chemical reactions of such olefines, it is evident that these reactions have been devised and applied chiefly for the purpose of isolation and identification, or for their removal as a nuisance, as for example, the usual method of refining with concentrated sulfuric acid.[102] It is, therefore, entirely possible that the discovery of new reactions will render these petroleum olefines industrially valuable.[103]

Octadienes: Conylene, C_8H_{44}. By distilling the ammonium base obtained by exhaustive methylation of coniine, an octadiene is obtained boiling at 126° (738 mm.). When benzoylconiine is treated with phosphorus pentachloride 1.5-dichlorooöctane is obtained.[104]

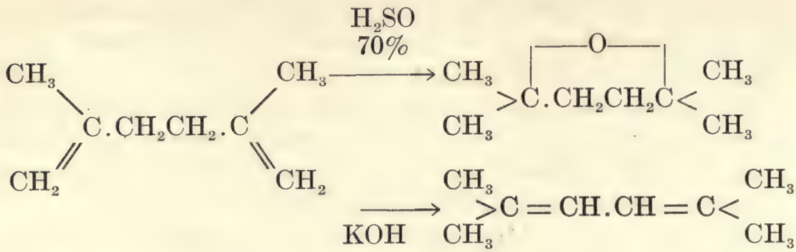
2.5-*Dimethylhexadiene*-(1.5)[105] is of interest as illustrating a property, quite general among dienes of eight or more carbon atoms, of forming an *oxide*, the anhydride of the 2.5-diol, when treated with 70 per cent sulfuric acid. This substance also illustrates the labil character of the α-olefine or $>C=CH_2$ group, being converted into diïsocrotyl by the action of alcoholic alkali,

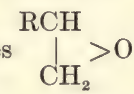
[102] That large proportions of the olefines remain in the refined oil as polymers, has previously been pointed out.

[103] The writer suggests that it would hardly be worth while, at least for one who greatly values his time, to enlarge our knowledge of the many possible hydrocarbons between pentane and the terpenes by proceeding along the old preparative lines, and examining the various derivatives by old reactions, and measuring the usual physical properties. Pending the possible development of new reactions, or greatly improved old ones, and the discovery of uses for such products as can now be made, it would seem that the best utilization of such olefines would be their polymerization, perhaps by aluminum chloride or zinc chloride to their much more stable polymers, of value as lubricants.

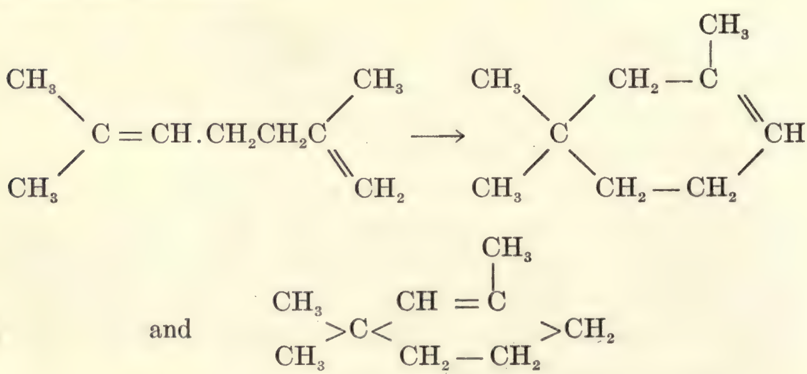
[104] v. Braun & Schmitz *Ber. 39*, 4366 (1906).

[105] Pogorzelsky, *J. Russ. Phys.-Chem Soc. 30*, 977 (1898); *J. Chem. Soc. Abs. 1899*, I. 785.



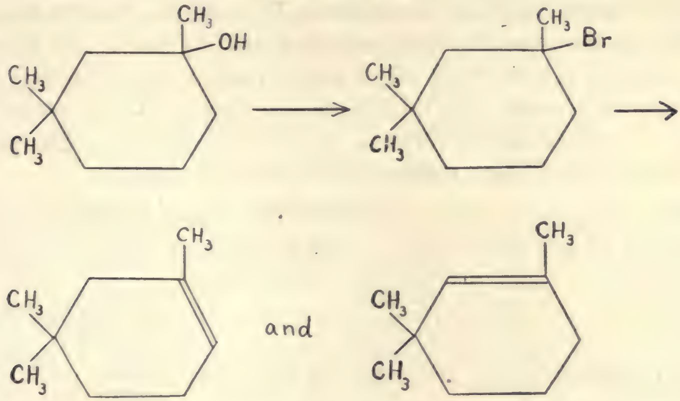
The latter hydrocarbon also yields this oxide when treated with 70 per cent sulfuric acid. (Oxides containing five or six atoms in the ring are very much more stable than the three membered ring oxides such as ethylene or propylene oxides  (Cf. Cineol.)

Nonadienes: Geraniolene, 2.6-Dimethylheptadiene-(1.5). This hydrocarbon, boiling-point 142°–143°, is of interest on account of its relation to geraniol and citral, and its conversion to cyclogeraniolene when treated with 65 per cent sulfuric acid. When the oxime of citral is dehydrated by acetic anhydride the nitrile is formed which readily yields geranic acid, $C_9H_{15}.CO_2H$. On distillation at ordinary pressure, geranic acid loses a molecule of CO_2 and forms "geraniolene."[106] The constitution of this hydrocarbon follows from the structure of citral and, if we accept the structure of citral as found by Barbier and Bouveault[107] the relations between geraniolene and α and β-cyclogeraniolene are as follows:



[106] Tiemann & Semmler, *Ber.* *26*, 2708 (1893).
[107] *Compt. rend.* *122*, 393 (1896).

Tiemanns' conclusions [108] as to the constitution of geraniolene and the cyclogeraniolenes are confirmed by Crossley and Gilling [109] by the synthesis of the supposed intermediate alcohol, and the conversion of the corresponding bromide into α and β-cyclogeraniolene.



Decadienes and Decatrienes: Dihydromyrcene, 2.6-Dimethylocta-diene (2.6). Boiling-point 166°–168°, $D^{15°}$ 0.7792.[110] This hydrocarbon is obtained by the partial hydrogenation of ocimene or myrcene, by means of sodium and alcohol,[111] or by slowly distilling methylgeranic acid.[112] Like geraniolene it is converted into a cyclic hydrocarbon by sulfuric acid (in acetic acid).[113] Kishner's method of converting aldehydes and ketones to hydrocarbons [114] converts citral to an isomer of dihydromyrcene, boiling-point 164.5°. Kishner's method reduces the carbonyl group to $-CH_2-$ without affecting the ethylene bonds present.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH.CHO$$

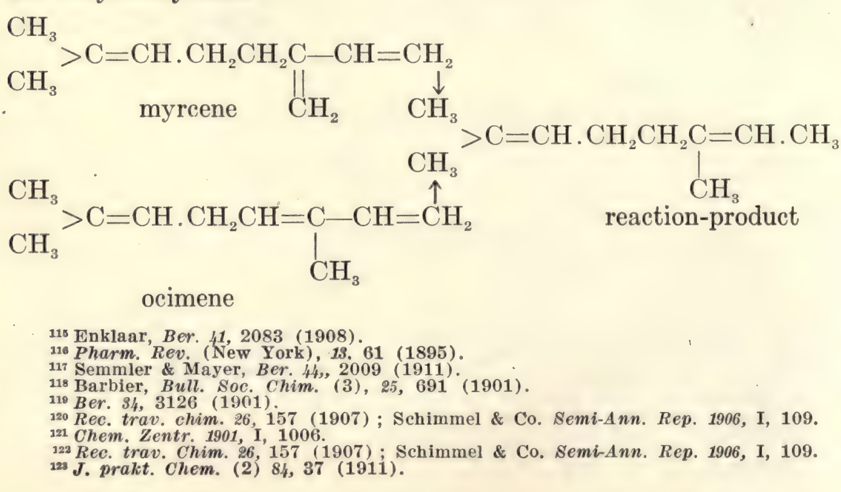
$$\longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH.CH_3$$

[108] *Ber. 31,* 816 (1898); *33,* 3711 (1900).
[109] *J. Chem. Soc. 97,* 2218 (1910). The above structures are also confirmed by the work of Wallach, *Ann, 324,* 97 (1902) but are not accepted by Harries and Turk, *Ann. 343,* 331, 362 (1905).
[110] Enklaar, *Rec. trav. chim. 26,* 164 (1907).
[111] Semmler, *Ber. 34,* 3126 (1910).
[112] Tiffeneau, *Compt. rend. 146,* 1154 (1908).
[113] *J. Russ. Phys.-Chem. Soc. 43,* 951 (1911).
[114] Enklaar, *Ber. 41,* 2083 (1908).

Myrcene, Ocimene and Alloöcimene: $C_{10}H_{16}$. These hydrocarbons are isomeric decatrienes, two of the double bonds being in conjugated positions. All three hydrocarbons yield 2.6-dimethyl octane on hydrogenation.[115] They are sometimes called "aliphatic terpenes" perhaps because of their empirical formulae $C_{10}H_{16}$ and the fact that myrcene and ocimene are constituents of essential oils. Myrcene was discovered by Power and Kleber [116] in oil of bay, *Pimenta acris* (Myrcia acris), one of the myrtaceae, and thus named by them. It also occurs in oil of hops [117] and in oil of verbena, *Lippia citriodoro*.[118] The physical properties of these three hydrocarbons are as follows:

Myrcene	*Boiling-Point*		*Density* $15°$	n_D
Power & Kleber	167°	: 67–68° 20mm.	0.8023	1.4673
Semmler [119]	171–172°	: 67–80° 20mm.	.....	1.4673
Enklaar [120]	166–168°		0.8013	1.4700
Ocimene			*Density* $15°$	n_D
Van Romburgh [121]	176–178°	: 73–74° 21mm.	0.801	1.4861
Enklaar [122]		81° 30mm.	0.8031	1.4857
Allo-Ocimene				
Auwers & Eisenlohr [123]	....	:	$0.8119\frac{15.6°}{4°}$	1.54558
Enklaar [122]	188°	: 81° 12mm.	0.8133	1.5447

Myrcene and ocimene, on partial hydrogenation, yield the same dihydromyrcene (dihydromyrcene tetrabromide melting-point 88°), and of the two original hydrocarbons myrcene is much more rapidly resinified. Enklaar proposed the following structures for myrcene, ocimene and dihydromyrcene.



[115] Enklaar, *Ber. 41,* 2083 (1908).
[116] *Pharm. Rev.* (New York), *13.* 61 (1895).
[117] Semmler & Mayer, *Ber. 44,,* 2009 (1911).
[118] Barbier, *Bull. Soc. Chim.* (3), *25,* 691 (1901).
[119] *Ber. 34,* 3126 (1901).
[120] *Rec. trav. chim. 26,* 157 (1907) ; Schimmel & Co. *Semi-Ann. Rep. 1906,* I, 109.
[121] *Chem. Zentr. 1901,* I, 1006.
[122] *Rec. trav. Chim. 26,* 157 (1907) ; Schimmel & Co. *Semi-Ann. Rep. 1906,* I, 109.
[123] *J. prakt. Chem.* (2) *84,* 37 (1911).

Ocimene derives its name from its presence in the essential oil of *Ocimum basilicum.*

Allo-ocimene was thought to be a geometrical isomer of ocimene, being obtained from this hydrocarbon by heating. Enklaar[124] later studied the ozonides and the resulting decomposition products of these hydrocarbons and concludes that allo-ocimene is

$$\begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\!\!\!\!\begin{array}{l} \\ >C=CH.CH=CH.\underset{\displaystyle |\atop\displaystyle CH_3}{C}=CH.CH_3 \\ \\ \end{array}$$

This structure having all three ethylene bonds in conjugated positions, as in n.hexatriene, accounts for the high refractivity of this hydrocarbon.

Both ocimene and myrcene yield alcohols, ocimenol and myrtenol, on treating with acetic acid and a trace of sulfuric acid, according to Bertram and Walbaum. Barbier[125] believes myrcenol to be different from linalool, and Enklaar noted the following constants: Boiling-point 99° (10 mm.), $d^{15°}$ 0.9032, $n^{15°}_{D}$ 1.4806, phenylurethane melting-point 68°. Ocimenol gives a phenylurethane melting at 72°. Enklaar is of the opinion that myrcene, ocimene and allo-ocimene are not obtainable in a state of purity, an opinion held by Wallach with regard to the terpinenes and phellandrenes. The instability of the former hydrocarbons probably accounts for the fact that the physical constants of the myrcene investigated by Lebedew and Mereshkowski[126] was found, after "repeated purification," to be quite different from the constants observed by others.[127]

Other Derivatives of 2.6-Dimethyloctane.

The Citral Group: Several well-known alcohols and aldehydes belong to this group. Their occurrence in essential oils is very wide and includes a very large number of plant species. Many of the most valuable essential oils owe their fine aroma chiefly to substances of this group, for example, the essential oils of the rose, *Rosa damascena* and *Rosa centifolia,* lavender and orange blossoms. Some of the cheaper oils such as lemon grass, citronella and palmrosa oils are used as raw

[124] *Rec. trav. chim.* 36, 215 (1916).
[125] *Bull. Soc. chim.* (3) 25, 687 (1901).
[126] *J. Russ. Phys.-Chem. Soc.* 45, 1249 (1913).
[127] The polymerizing action of metallic sodium on conjugated dienes is now well known; such hydrocarbons give a brown resinous deposit after repeated distillation over sodium.

materials for the isolation of certain constituents such as citral and geraniol, which are further utilized, as in the manufacture of ionone from citral. The chemical behavior of these alcohols and aldehydes has been well established but in most cases it has been impossible definitely to distinguish between the groups

$$\begin{matrix} CH_3 \\ & \searrow \\ & & C = CHR \\ & \nearrow \\ CH_3 \end{matrix} \quad \text{and} \quad \begin{matrix} CH_3 \\ & \searrow \\ & & C.CH_2R. \\ & /\!/ \\ CH_2 \end{matrix}$$

Instead of outlining the historical development of the subject, the general relationships of the substances in this group will be indicated, followed by a description of the individual substances and some of their more important reactions.

The chemical behavior and constitution of substances in the citral series is intimately associated with methylheptenone,[128] or, as Tiemann and Semmler[129] showed it to be, 2-methylheptene-(2)-one-(6), $(CH_3)_2 = CH.CH_2CH_2COCH_3$. A little later, Verley [130] confirmed this structure by synthesis. Oxidation, first by Wagner's method, using cold dilute permanganate, followed by chromic acid, yields acetone, and levulinic acid.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C \vdots = CH.CH_2CH_2COCH_3 \longrightarrow (CH_3)_2CO + \begin{matrix} CH_2COCH_3 \\ | \\ CH_2CO_2H \end{matrix}$$

On boiling an aqueous solution of potassium carbonate with *citral* methylheptenone and acetaldehyde are formed, and on oxidizing with chromic acid methylheptenone is also produced. The empirical formula of citral is $C_{10}H_{16}O$ and its chemical behavior and physical properties indicate that it is an aldehyde containing two double bonds. If methylheptenone condensed with acetaldehyde, splitting off a molecule of water as in the condensation of acetaldehyde to croton aldehyde, or acetone to mesityl oxide,

$$CH_3\,CHO + CH_3CHO \longrightarrow CH_3CH = CH.CHO$$

[128] Methylheptenone is usually associated with citral, and is a constituent of lemon grass, lemon, palmarosa and linaloe oils. It is best prepared by boiling a 10% solution of potassium carbonate with citral, Verley, *Bull. Soc. chim.* (3) *17,* 176 (1897). Its boiling-point is 173°-174°; density 20° 0.8602. Hydrogen in the presence of nickel at 180°-190° saturates only the double bond; sodium and alcohol reduces the ketone group forming methyl heptenol. It reacts normally with alkyl magnesium halides.

[129] *Ber. 28,* 2115, 2126 (1895).

[130] *Bull. Soc. chim. 17,* 192 (1897).

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CO + H_2CH.COCH_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.COCH_3$$

the result would be citral. Such a reaction would be the reverse of the hydrolytic reaction brought about by aqueous potassium carbonate.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C} = CH.CHO \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C} = O$$

citral $+ CH_3CHO$

That this is the structure of citral is indicated by the synthesis of geranic acid from methylheptenone [131] and the conversion of geranic acid to citral by heating its calcium salt with calcium formate.[132] Methylheptenone and iodoacetic ester condense in the presence of zinc to give the hydroxy acid and heating this with acetic anhydride yields geranic acid.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C} = O + CH_2I.CO_2R \longrightarrow$$

$$\longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C}\!\!<\!\begin{matrix} OZnI \\ CH_2CO_2H \end{matrix} \longrightarrow \text{hydroxy acid}$$

$$\longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C} = CH.CO_2H \longrightarrow$$

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C = CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C} = CH.CHO$$

citral

Tiemann [133] discovered that purified natural citral yields mainly a semicarbazone melting at 164°, and from the mother liquors of these crystals a second semicarbazone melting at 171° was isolated; mixtures of the two melt as low as 130°. The aldehyde yielding the low melting

[131] Barbier & Bouveault, *Compt rend.* **122**, 393 (1896).
[132] Tiemann, *Ber.* **31**, 827 (1898).
[133] *Ber.* **31**, 3331 (1898); **32**, 115 (1899); **33**, 877 (1900).

semicarbazone was designated "citral *a*" and the other "citral *b*." Citral *a* condenses more readily with cyanacetic acid, forming a citrylidene cyanacetic acid melting at 122° and the corresponding derivative of citral *b* melts at 94°–95°. Tiemann considered these isomeric crystalline derivatives as geometrical isomers and Zeitschel [134] states that citral *a* and citral *b* probably correspond to the geometrically isomeric alcohols geraniol and nerol.

$$\begin{array}{rcl}
\begin{array}{r} Me_2C = CH.CH_2CH_2C - CH_3 \\ \| \quad\quad\quad \\ HC - CH_2OH. \end{array} & \rightarrow & \begin{array}{r} Me_2C = CH.CH_2CH_2C - CH_3 \\ \| \quad\quad\quad \\ HC.CHO \end{array} \\
\text{geraniol} & & \text{citral } a \\
\begin{array}{r} Me_2C = CH.CH_2CH_2C - CH_3 \\ \| \quad\quad\quad \\ HO.H_2C - C - H. \end{array} & \rightarrow & \begin{array}{r} Me_2C = CH.CH_2CH_2C - CH_3 \\ \| \quad\quad\quad \\ OHC - C - H \end{array} \\
\text{nerol} & & \text{citral } b
\end{array}$$

Citral *a* and citral *b* have practically the same chemical properties [135] and their physical properties differ only very slightly. As a rule, the boiling-points of such geometrical isomers differ only very slightly, for example, the two β-butylenes, and dibromobutylenes

$$\begin{array}{llll}
\begin{array}{l} HC - CH_3 \\ \| \\ HC - CH_3 \end{array} & \begin{array}{l} \text{boiling-point} \\ \\ +1^\circ \text{ to } 1.5^\circ \end{array} & \begin{array}{r} HC - CH_3 \\ \| \quad\quad \\ CH_3 - C - H \end{array} & \begin{array}{l} \text{boiling-point} \\ \\ +2^\circ \text{ to } 2.7^\circ \end{array} \\
\begin{array}{l} Br - C - CH_3 \\ \| \\ Br - C - CH_3 \end{array} & \begin{array}{l} \text{boiling-point} \\ \\ 146^\circ\text{–}146.5^\circ \end{array} & \begin{array}{r} Br - C - CH_3 \\ \| \quad\quad \\ CH_3 - C - Br \end{array} & \begin{array}{l} \text{boiling-point} \\ \\ 149^\circ\text{–}150^\circ \end{array}
\end{array}$$

That small differences in structure may greatly affect the melting point has previously been pointed out, and the different melting points of certain derivatives of these isomeric citrals is a case in point. Conversion of citral *a* to citral *b* and vice versa takes place readily, and, according to Bouveault,[136] alkalies convert *a* to *b*. Ordinary natural citral gives nearly pure condensation products of citral *a*.

Further confirmation of the above relationship of geraniol and nerol is found in the behavior of these two alcohols on oxidation, first by dilute permanganate thus oxidizing the double bonds to glycols, and followed by oxidation with chromic acid. Both alcohols yield the same oxidation products and in the same proportions, i. e., acetone, levulinic

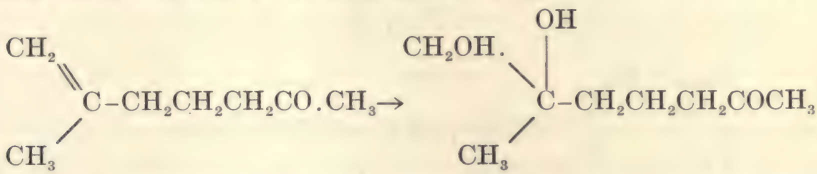
[134] *Ber.* *39,* 1780 (1906).
[135] Tiemann, *Ber.* *33,* 877 (1900).
[136] *Bull. Soc. chim.* (3), *21,* 423.

acid and oxalic acid.[137] As in the case of the two citrals, geraniol and nerol have nearly identical physical properties but the melting-points of some of their condensation products differ markedly.

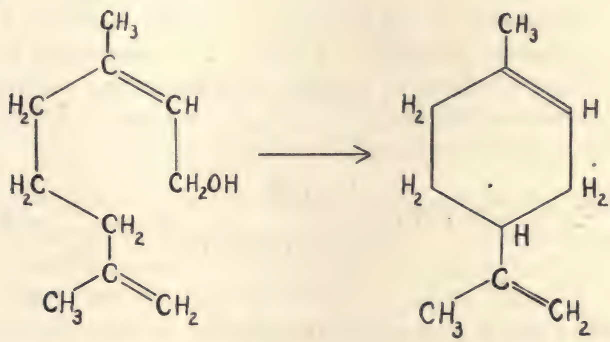
	Geraniol[138]	*Nerol*[139]
Boiling-point	230°	226°–227°
" "	110°–111° (10mm.)	111° (9mm.)
Specific gravity	0.8812 to $0.883^{15°}$	$0.8813^{15°}$
Refractive index	1.4766 – 1.4786	1.468
Diphenylurethane, M. P........	82.5°	52°–53°
Tetrabromide, M. P............	70°–71°	118°–119°

Separation of geraniol and nerol is best carried out by means of anhydrous calcium chloride which forms a crystalline product with geraniol but not with nerol.

According to a recent paper by Verley,[140] citral *a* is mainly the Δ^1 isomer. When it is boiled with one per cent aqueous caustic soda 2-methyl-Δ^1-heptenone is produced, which when oxidized first by permanganate and then by chromic acid gives only traces of acetone,



This methylheptenone is rapidly converted into the isomeric, ordinary 2-methyl-Δ^2-heptenone, by warming with dilute sulfuric acid. Verley therefore favors the corresponding Δ^1 formula for geraniol and points out that this structure better explains the conversion of geraniol to dipentene.



[137] Blumann & Zeitschel, *Ber.* *44*, 2590 (1911).
[138] Bertram & Gildemeister, *J. prakt. Chem.* (2) *56*, 508 (1897); Erdmann, *J. prakt. Chem.* (2) *56*, 3 (1897); Stephan, *ibid.*, *58*, 110 (1898).
[139] Soden & Treff, *Chem. Ztg.* *27*, 897 (1903).
[140] *Bull. Soc. chim.* (4), *25*, 68 (1919).

Two ketones occurring in artemisia oil appear to have a carbon structure different from the citral group but these two isomeric ketones are supposed to bear the same relation to each other as the Δ^1 and Δ^2 isomers discussed above.[141]

As is indicated in the foregoing discussion of the constitution of citral, the constitution of geraniol and nerol are shown by their relations to citral. Citral is formed from geraniol by oxidation with chromic acid,[142] and reduction of citral yields geraniol. Apparently only the groups $-CH_2OH$ and $-CHO$ are affected. On more energetic oxidation the citral first formed is oxidized as indicated above, to methylheptenone, acetone, levulinic acid, etc. These relations are, therefore, expressed by the following constitutions of geraniol,

$$\begin{array}{l} CH_3 \\ \quad\diagdown \\ \qquad C = CH.CH_2CH_2\underset{\displaystyle \begin{array}{c}|\\ CH_3\end{array}}{C} = CH.CH_2OH \\ \quad\diagup \\ CH_3 \end{array}$$

$$\text{or,}\qquad \begin{array}{l} CH_3 \\ \quad\diagdown \\ \qquad C.CH_2CH_2CH_2\underset{\displaystyle \begin{array}{c}|\\ CH_3\end{array}}{C} = CH.CH_2OH \\ \quad /\!/ \\ CH_2 \end{array}$$

When geraniol is heated with water in an autoclave to 200° linalool is formed,[143] and the conversion of linalool to geraniol, or geranyl acetate is brought about by heating with acetic anhydride.[144] By warming a solution of linalool in toluene with hydrochloric acid, geranyl chloride is formed.[145] These changes are readily understood from the structure of linalool deduced by Tiemann and Semmler [146] by a study of the oxidation products of linalool. Oxidizing first with dilute permanganate, followed by chromic acid gave acetone and levulinic acid (equivalent to methylheptenone) and *oxalic acid.*

$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>C = CH.CH_2CH_2C\!\!<\!\begin{array}{l} OH \\ .CH = CH_2 \end{array} \atop \qquad\qquad\qquad\qquad\quad |\;\; \atop \qquad\qquad\qquad\qquad\quad CH_3 \quad \longrightarrow \quad \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CO +$$

[141] Asahina & Takagi, *J. Chem. Soc. Abs. 1921,* I. 9.
[142] Semmler, *Ber. 23,* 2966 (1890).
[143] *Schimmel & Co.'s Ber. 1898,* I, 25.
[144] Bouchardat, *Compt. rend. 116,* 1253 (1893). Terpineol is also formed.
[145] Tiemann, *Ber. 31,* 832 (1898); Dupont & Labaune, *Roure-Bertrand, Fils. Bull. 1909,* II. 27; Forster & Cardwell, *J. Chem. Soc. 103,* 1338 (1913).
[146] *Ber. 28,* 2126 (1895).

$$\underset{\displaystyle\;CH_3}{CO_2H.CH_2CH_2\overset{}{C}O} \quad + \quad \begin{array}{c} CO_2H \\ | \\ CO_2H \end{array}$$

It was also pointed out that the chemical and physical properties of linalool agree with the structure of a tertiary alcohol, and that when oxidized by chromic acid direct, to citral, isomerization by the acid to geraniol, or the glycol, first takes place,

$$\text{linool} \xrightarrow{\text{by acid}} \text{geraniol} \xrightarrow{CrO_3} \text{citral}$$

$$\begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\!\!>C = CH.CH_2CH_2\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH = CH_2 \longrightarrow R\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - CH_2 - CH_2OH$$

linalool

$$\longrightarrow R - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH.CH_2OH \longrightarrow R\underset{\displaystyle CH_3}{\underset{|}{C}} = CH.CHO$$

geraniol citral

Linalool has recently been synthesized by Ruzicka[147] who employed a reaction discovered by Nef,[148] i. e., condensation of acetylene with ketones by means of metallic sodium. The first condensation product gives good yields of linalool on reducing by moist ether at low temperatures.

$$\begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\!\!>C = CHCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CO + HC \equiv CH$$

$$\longrightarrow \begin{array}{l} CH_3 \\ \\ CH_3 \end{array}\!\!>C = CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}\!<\!\begin{array}{l} OH \\ C \equiv CH \end{array} \longrightarrow \text{linalool}$$

The constitution of citronellol and the corresponding aldehyde, citronellal, is shown by the following reactions; citral may be oxidized to the corresponding acid geranic acid and on reducing this by sodium and amyl alcohol *citronellic* acid is obtained; also the aldehyde citronellal may be converted to its oxime and this, by loss of H_2O, to the nitril, which yields citronellic acid. Therefore, citronellol is dihydrogeraniol,

[147] *Helv. Chim. Acta.* **2**, 182 (1919).
[148] *Ann.* **308**, 264 (1898).

and citronellal is dihydrocitral.[149] As to the location of the remaining double bond in citronellic acid, citronellol and its aldehyde, the evidence was at first confusing, but the facts are best explained by the reduction of the $\begin{array}{l}\mathrm{RC=CH.COOH} \\ \;\,| \\ \mathrm{\;CH_3}\end{array}$ group, which is in harmony with the well known highly reactive character of the $>\mathrm{C=C-CO-}$ group. The aldehyde citronelall can be reduced mainly to the corresponding alcohol, citronellol, by sodium amalgam in acetic acid.[150] As with the other substances of this group, some doubt remains as to whether the double bond in citronellol and its aldehyde is in the position shown but according to Harries [151] both isomers are present in natural citronellol, i. e.,

$$\begin{array}{l}\mathrm{CH_3} \\ \quad\diagdown \\ \qquad\mathrm{C=CH.CH_2CH_2CH.CH_2CH_2OH} \\ \quad\diagup \qquad\qquad\qquad\qquad\;\; | \\ \mathrm{CH_3} \qquad\qquad\qquad\qquad\;\; \mathrm{CH_3}\end{array}$$

and

$$\begin{array}{l}\mathrm{CH_3} \\ \quad\diagdown \\ \qquad\mathrm{C-CH_2CH_2CH_2CH.CH_2CH_2OH.} \\ \quad /\!/ \qquad\qquad\qquad\qquad\quad | \\ \mathrm{CH_2} \qquad\qquad\qquad\qquad\quad \mathrm{CH_3}\end{array}$$

Citronellol and *rhodinol* appear to be isomers differing only in the position of the double bond,

$$\begin{array}{l}\mathrm{CH_2} \\ \quad\diagdown\!\!\diagdown \\ \qquad\mathrm{C.CH_2R}, \text{ or } \mathrm{(CH_3)_2C=CH.R.} \\ \quad\diagup \\ \mathrm{CH_3}\end{array}$$

The question of the existence of rhodinol has been the subject of considerable controversy, the difficulty of deciding such questions being that, as in all such cases, the chemical behavior and physical properties are so nearly identical, and conversion of the one isomer into the other takes place with great ease. In discussing the simple aliphatic olefines, such as hexene(1), it was pointed out that double bonds of the type $\mathrm{RCH_2CH=CH_2}$ frequently shift their position very readily, and the work of Verley, noted above, shows that warming with dilute sulfuric acid changes the group

[149] Tiemann, *Ber. 31,* 2899 (1898); Bouveault, *Compt rend. 138,* 1699 (1904).
[150] Dodge, *Am. Chem. J. 11,* 463 (1889).
[151] *Ber. 41,* 287 (1908).

$$\begin{array}{l} CH_2 \\ \quad \backslash\backslash \\ \qquad C.CH_2R \text{ to the isomer } (CH_3)_2C = CH.R. \\ \quad / \\ CH_3 \end{array}$$

German chemists continued to regard rhodinol as a mixture of citronellol and geraniol but Harries [152] and his assistants have shown that natural citronellol and the aldehyde citronellal consists of a mixture of the two isomers, confirming the contention of Barbier, Bouveault [153] and Locquin [154] as to the existence of rhodinol. According to Harries ordinary citronellal, derived from oil of citronella, contains approximately 60 per cent "rhodinal," the aldehyde corresponding to rhodinol. Methods of oxidation have not clearly shown the structure of these isomers but rhodinol appears to be the more stable of the two alcohols. Both alcohols, in the form of their acetates, combine with hydrogen bromide, and when this is removed by heating with sodium acetate, rhodinol is the product. Also, according to Barbier and Locquin,[155] citronellal may be converted into its oxime, which on dehydrating by acetic anhydride yields the nitrile, but the oxime of the aldehyde, made by the oxidation of *l*-rhodinol or *d*-rhodinol, does not yield the nitrile but acetylmenthone oxime. Citronellol may be converted into rhodinol by the addition of water, brought about by treating with 30 per cent sulfuric acid.

$$\begin{array}{l} CH_2 \\ \quad \backslash\backslash \\ \qquad C.CH_2CH_2CH.CH_2.CH_2OH \qquad \text{citronellol} \\ \quad / \qquad\qquad\quad | \\ CH_3 \qquad\qquad\quad CH_3 \end{array}$$

$$\downarrow$$

$$\begin{array}{l} CH_3 \\ \quad \backslash \\ \qquad C.CH_2CH_2CH_2CH.CH_2CH_2OH \\ \quad / \;| \qquad\qquad\qquad | \\ CH_3 \;\; OH \qquad\qquad\quad CH_3 \end{array}$$

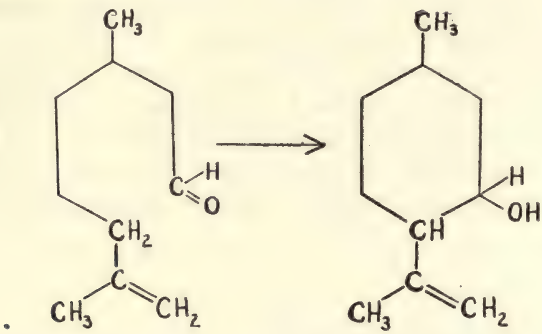
$$\downarrow$$

$$\begin{array}{l} CH_3 \\ \quad \backslash \\ \qquad C = CH.CH_2CH_2CH.CH_2.CH_2OH \\ \quad / \qquad\qquad\qquad\quad | \\ CH_3 \qquad\qquad\qquad\quad CH_3 \end{array}$$

rhodinol (according to Barbier).

[152] *Ber.* 41, 2187 (1908); *Ann.* 410, 1 (1915).
[153] *Bull. Soc. chim.* (3), 23, 458, 465 (1900).
[154] *Compt. rend.* 157, 1114 (1913).
[155] *Loc. cit.*

Prins [156] endeavored to separate natural citronellal into its two isomers, by repeated fractional distillation [157] followed by repeated fractional crystallization of the semicarbazone and semioxamazone, but without success. Prins also studied the conversion of citronellal to isopulegol, by treating with 85 per cent formic acid and by 80 per cent phosphoric acid but was unable to detect the formation of any substance, which could be derived directly from rhodinal. The formation of isopulegol acetate by heating ordinary citronellal with acetic anhydride is practically quantitative,[158] which, in the light of Harries' work, indicates that under these conditions rhodinal must be converted into its isomer, true citronellal. Barbier and Bouveault believed that they had obtained small yields of menthone from rhodinal, but Tiemann and Schmidt [159] were unable to confirm this. The ready conversion of citronellal to isopulegol, however, favors the structure purposed by Barbier for this aldehyde,



According to Semmler [160] aldehydes of the types $R_2CH.CHO$ and RCH_2CHO are converted to enolic forms by acetic anhydride and that in the case of citronellal this change precedes ring formation.

The above review illustrates how difficult it is to distinguish between isomers of this kind.

Geraniol. The importance of the alcohols and aldehydes of this group to the essential oil industry warrants further description of them and their chemical behavior. Geraniol is present to a large extent in palmarosa oil, ginger grass, citronella and oil of sweet geranium, partly

[156] *Chem. Weekbl.* *14*, 627, 692 (1917). The maximum difference in boiling-points observed by Prins was 198°-200° for the low-boiling fraction and 203°-204° for the higher boiling portion.

[157] *Schimmel & Co.'s Rep. 1910*, I, 155.

[158] *Schimmel & Co.'s Rep. 1896*, 34; Semmler, *Ber. 42*, 584, 963, 1161, 2014 (1909).

[159] *Ber. 30*, 38 (1897).

[160] *Ber. 42*, 584, 963, 1161, 2014 (1909); *44*, 991 (1911).

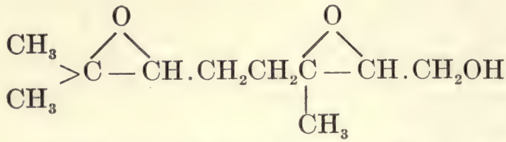
in the free state and partly as the acetate. In oil of geranium small proportions of the geraniol ester of tiglic acid are present.[161] Commercially geraniol is isolated from either palmarosa or citronella oil by means of finely ground anhydrous calcium chloride, the mixture being chilled to about $-5°$ for several hours. Other oils are removed by means of petroleum ether and the crystalline calcium chloride compound decomposed by water. Small percentages of geraniol cannot be separated from essential oils in this manner. It is readily identified by its diphenylurethane,[162] melting-point 82°, or its naphthylurethane, melting-point 47°–48°.

Geranyl chloride is of particular interest as filling a niche in the chemistry of the non-benzenoid hydrocarbons and contributing to the generally similar chemical behavior of this whole class of substances. Although not mentioned in Richter's "Lexikon" geranyl chloride was evidently first made by Jacobsen[163] and later by Tiemann[164] who prepared large quantities of it by the action of hydrogen chloride on geraniol. Dupont and Labaune[165] passed dry hydrogen chloride into a solution of geraniol or linalool in toluene at 100° and noted that both alcohols gave the same chloride, which they called linalyl chloride, and Kerschbaum[166] following Tiemann's first method, made it by treating geraniol with phosphorus trichloride. The first study of the chloride and its reactions was carried out by Forster and Cardwell,[167] who employed Darzen's method, dissolving the geraniol in pyridine and treating with thionyl chloride. The chloride was shown to be a derivative of geraniol rather than linalool by the preparation of geranyl acetone, by the action of geranyl chloride on the sodium derivative of acetoacetic ester, and hydrolysis of the geranyl acetoacetate by barium hydroxide. The constitution of geranyl acetone is shown by reference to the constitution of farnesol[168] and the work of Kerschbaum.[169] The chlorine atom in geranyl chloride is stabilized by the proximity of a double bond, $(CH_3)C = CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CH.CH_2Cl$ but it reacts normally with sodium ethoxide to give the ethyl ether and with sodium acetoacetic ester and sodium malonic ester. From the latter substance

[161] Schimmel & Co., *Semi-Ann. Rep.* *1913*, II, 61.
[162] Cf. Parry, "Essential Oils" Vol. II, Ed. II, *1919*, 98.
[163] *Ann.* *157*, 236 (1871).
[164] *Ber.* *29*, 921 (1896) ; *31*, 832 (1898).
[165] *Roure-Bertrand Fils' Bull.* *1909*, II, 19.
[166] *Ber.* *46*, 1735 (1913).
[167] *J. Chem. Soc.* *103*, 1338 (1913).
[168] Harries & Haarman, *Ber.* *46*, 1737 (1913).
[169] *Loc. cit.*

geranyl acetic acid was made, $C_{10}H_{17}.CH_2CO_2H$. Sodium azide yields the azoimide and corresponding amine, geranyl amine.

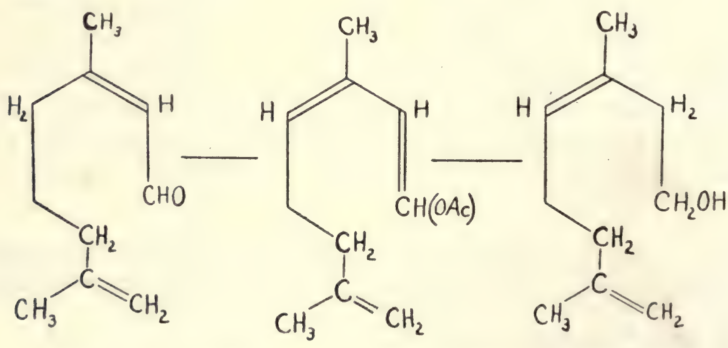
Prileshajev [170] has prepared the mono and dioxides of geraniol by direct oxidation by benzoyl peroxide. The dioxide is a mobile liquid boiling at 180°–183° under 25 mm.



geraniol dioxide (according to Prileshajev)

Geraniol is markedly less stable than citronellol. On heating with phthalic anhydride to 200° geraniol is decomposed but citronellol forms the acid phthalic ester; concentrated formic acid also decomposes geraniol much more readily than citronellol.[171] Benzoyl chloride at 140°–160° also decomposes geraniol,[172] but not citronellol.

Isogeraniol: Evidence of a shift in the position of one double bond in citral by the action of acetic anhydride is furnished by the isolation of an *isomer* of geraniol when the acetic ester of enol-citral is reduced by sodium amalgam in methyl alcohol acidified by acetic acid.[173] This alcohol, like geraniol, has a fine roselike odor and may be distinguished by means of its diphenylurethane melting at 73°. According to Semmler, the formation of isogeraniol may be represented as follows:



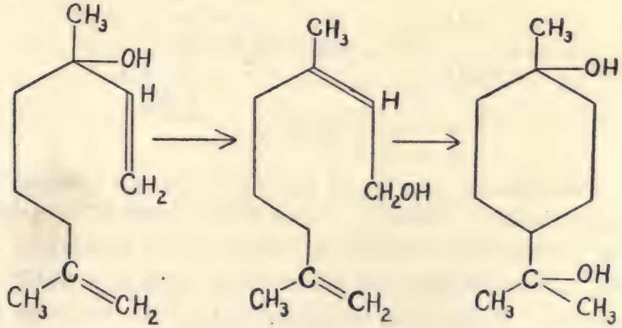
[170] *J. Russ. Phys.-Chem. Soc.* *44*, 613 (1912); a trace of mineral acid hydrolyses one of the oxide groups, forming the glycol, $C_{10}H_{17}O.(OH)_3.2H_2O$ melting-point 94.5°, also the anhydrous glycol $C_{10}H_{17}O.(OH)_3$ in two forms melting at 145° and 163°.

[171] Walbaum & Stephen, *Ber.* *33*, 2307 (1900).

[172] Barbier & Bouveault, *Compt. rend.* *122*, 530 (1896).

[173] Semmler, *Ber.* *44*, 991 (1911).

Linalool: Linalool is isolated technically from oil of Central American linaloe wood. Its acetate is the principal constituent of oil of lavender and it is an important component of a great number of other essential oils, among which are ylang-ylang, champaca, rose, geranium, petit-grain, bergamot, neroli, jasmine and other oils. It is not easily isolated or purified since it yields no crystalline addition products or derivatives from which linalool can easily be regenerated. Hydrogen chloride forms geranyl chloride, boiling-point 82°–86° at 6 mm.[174] Mono linalyl phthalate may be prepared by forming the sodium compound of linalool, in ether and allowing this to stand several days with phthalic anhydride.[175] Linalool, being a tertiary alcohol, is partially decomposed when acetylation by acetic anhydride is attempted, dipentene, terpinene, α-terpinyl acetate and neryl acetate being formed.[176] Continued heating with acetic anhydride decomposes terpineol, also a tertiary alcohol, and maximum yields of terpinyl acetate, about 85 per cent, are obtained in 45 minutes.[177] When diluted with xylene, as proposed by Baulez, the maximum esterification, about 63 per cent, is obtained in 7 hours.[178] The conversion of linalool to terpinene and dipentene by heating with acids is believed to involve isomerization to geraniol.



Anhydrous oxalic acid is much more energetic in its action and yields a bicyclic diterpene, $C_{20}H_{32}$, isocamphorene.[179]

Oxidation of linalool by benzoyl yields a mono oxide or dioxide depending upon the proportions of benzoyl peroxide employed[180] and

[174] Forster & Cardwell, *loc. cit.*
[175] Charabot, *Ann. chim. phys.* (7), *21*, 232 (1901).
[176] Stephan, *J. prakt. Chem.* (2), *58*, 109 (1898); Zeitschel, *Ber. 39*, 1780 (1906).
[177] Schimmel & Co.'s *Ber. 1893*, I, 38.
[178] Schimmel & Co.'s *Ber. 1907*, I, 127.
[179] Semmler, *Ber. 47*, 2068 (1914).
[180] Prileshajev, *loc. cit.* The oxide of linalool found in lanaloe oil by Schimmel & Co. [*Semi-Ann. Rep. 1912* (2), 78] boils at 197°-198° (758 mm.) and is not readily hydrolyzed by dilute acids indicating clearly that the oxygen is not attached to

H. Erdmann[181] employed linalyl acetate in studying the addition of sulfur to unsaturated substances to form what he terms thioözonides. These thioözonides decompose on heating, evolving hydrogen sulfide.

A tertiary alcohol resembling linalool and containing two more hydrogen atoms (one less double bond) has been prepared by two well-known reactions, which have previously been discussed in connection with the synthesis of hydrocarbons, and the action of sulfuric acid upon olefines. Thus dihydromyrcene on treating with 85 per cent sulfuric acid[182] yields *dihydrolinalool;* the same tertiary alcohol is obtained by the action of ethyl magnesium bromide on methyl heptenone.

$$(1)\quad \text{myrcene} \xrightarrow{+H_2} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C}=CH.CH_3 \xrightarrow{+H_2O}$$

$$(2)\quad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C}=O + C_2H_5MgBr \longrightarrow$$

$$\longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.CH_2CH_2\underset{\substack{|\\ CH_3}}{C}\!\!<\!\begin{matrix} CH_2CH_3 \\ OH \end{matrix}$$

dihydrolinalool.

Contrary to opinions previously held, Dupont and Labaune[183] find that the double bonds in linalool and geraniol react with sodium sulfite. These alcohols are completely dissolved by continued shaking with aqueous sodium sulfite, the compounds $C_{10}H_{18}O.2NaHSO_3$ having been isolated. It has long been known that the ethylene bond in citral, in the group $-\underset{\substack{|\\ CH_3}}{C}=CH.CHO$ reacts readily with sodium sulfite, but this is the first instance of unsaturated alcohols reacting in this manner.

Citronellol and Rhodinol: From the foregoing discussion of these

adjacent carbon atoms. The oxide of linalyl acetate, made by Prileshajev's method, reacts with water readily to give the glycol $C_{10}H_{17}(OH)_2.O_2C_2H_3$ which on saponification yields $C_{10}H_{17}(OH)_3$ melting at 54°-55°.

[181] *Ann.* *362,* 137 (1908)

[182] Myrcene is converted to *cyclo* dihydromyrcene by the action of sulfuric acid in acetic acid.

[183] *Roure-Bertrand Fils' Bull. 1912,* (3) *6 & 7; J. Chem. Soc. 1913,* I, 746.

two substances it is evident that these two alcohols occur together, and while recognizing the probable existence of rhodinol, the name citronellol will be retained and, following common usage, will be employed for the alcohol $C_{10}H_{20}O$, containing one double bond, and having the following physical properties:

PHYSICAL PROPERTIES.

Observer	*Boiling-Point*	*Density*	n_D	*Method of Isolation*
Wallach[184]	114°–115° (12–13mm.)	$0.856\frac{22°}{}$	1.4561	Destroying geraniol at 250°
Tiemann[185]	117°–118° (17mm.)	$0.8565\frac{17°}{}$	1.4566	reduction of citronellal
Tiemann[186]	113°–114° (15mm.)	$0.8612\frac{20°}{}$	1.4578	by PCl_3 method
Schimmel & Co.[187]	225°–226°	0.862	1.45611	Wallach's method
Schimmel & Co.[188]	109° (7mm.)	0.8604 0.8629	1.4565 1.4579	From Java citronella
Schimmel & Co.	225°–226°	0.862 0.869	1.459 1.463	Commercial preparation from oil of geranium

Citronellol is considerably more stable than geraniol or linalool, to the action of alkalies, 10 per cent sulfuric acid, heating with formic acid or phthalic anhydride, phosphorus trichloride in the cold, heating with water as in Wallach's method of purifying citronellol. The formation of a cyclic hydrocarbon by loss of water from citronellol has not been observed.

Citral: The constitution of citral and the nature of citral *a* and citral *b* have been discussed in the preceding general discussion. The following physical properties of citral have been noted:

Observer	*Boiling-Point*	*Density*	n_D	*Source*
Tiemann & Semmler[189]	110°–112° (12mm.) 117°–119° (20mm.)	$0.8972\frac{15°}{}$	1.4931	....
Schimmel & Co.[190]	110°–111° (12mm.)	$0.893\frac{15°}{}$	1.4901	lemon-grass
Schimmel & Co.	92°– 93° (5mm.)	$0.8926\frac{15°}{}$	1.4885	lemon

[184] *Nachr. K. Ges. Wiss. Göttingen, 1896*, 56.
[185] *Ber. 29*, 906 (1896).
[186] Ibid, 923.
[187] *Schimmel & Co.'s Ber. 1898*, 62.
[188] Ibid, *1902*, I, 14.
[189] *Ber. 26*, 2709 (1893).
[190] *Schimmel & Co. Rep. 1899*, I, 72.

In addition to the chemical reactions of citral noted above, the following may be noted. Potassium acid sulfate or moderately diluted sulfuric acid react on citral very energetically with ring closing, loss of water and the formation of p.cymene.

The behavior of citral to sodium sulfite solutions has been the subject of considerable investigation. In the presence of a very slight excess of free sulfurous acid, in the cold, the normal, aldehyde addition product $C_9H_{15}CH<\begin{matrix}OH\\OSO_2Na\end{matrix}$ is formed, separating as very fine, sparingly soluble, crystalline plates; regeneration of citral from this derivative is not quantitative. If this crystalline product is allowed to stand, and gently warmed, with an excess of bisulfite, it goes into solution as a *labil* dihydrodisulfonic acid derivative, from which citral can be regenerated by the action of caustic soda, but not by alkali carbonates. If the bisulfite solution of citral is strongly heated, the *stabil* dihydrodisulfonic acid derivative is formed and it is impossible to regenerate citral from this stabil combination. If the *labil* dihydrodisulfonic acid salt is treated with another molecular portion of citral, this goes into solution as a labil *mono*hydrosulfonate which can readily be decomposed to citral. The formation of labil soluble sulfonate of citral can also be carried out by employing neutral sodium sulfite and neutralizing the free alkali, as fast as formed, by acetic acid.[191]

$$C_9H_{15}CHO + 2Na_2SO_3 + 2H_2O \rightarrow C_9H_{15}CHO.(NaHSO_3)_2 + 2NaOH$$

This reaction usually gives so much difficulty that Tiemann's [192] directions may be given here. A solution of 350 g. sodium sulfite in one liter of water is made slightly alkaline to phenolphthalein, treated with 100 g. citral and gently shaken, keeping just slightly alkaline by the continual addition of a calculated quantity of 20 per cent sulfuric acid (or acetic acid). The solution should always be distinctly red by phenolphthalein, since in slightly acid solution the sparingly soluble crystalline compound will separate. The various addition products formed by sodium bisulfite and citral may be summarized thus,[193] where X represents the SO_3Na group. Evidently, in the stable derivatives, carbon and sulfur are directly combined as — C — SO_3Na or true sulfonic acid salts.

[191] Cf. Gildemeister, *"Die Aetherischen Oele,"* Vol. I. Ed. II. 429—(1910).
[192] *Ber. 31,* 3317 (1898).
[193] G. Romeo, *Gazz. chim. Ital. 48,* (1), 45 (1918).

(1) normal aldehyde addition product.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}=CH.CH\!<\!\!\begin{matrix} OH \\ OSO_2Na \end{matrix} \qquad \textit{labil.}$$

(2) stable dihydrodisulfonate, formed in warm acid solutions, probably of the type $-C-SO_3Na$.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\overset{(HX)}{C}-CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{(HX)}{C}}}-CH.CHO \qquad \textit{stable.}$$

(3) labil dihydrodisulfonate, formed in slightly alkaline solutions, probably of the type $-C-OSO_2Na$.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\overset{(HX)}{C}-CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{(HX)}{C}}}-CH.CHO \qquad \textit{labil.}$$

(4) Citral *mono* sodium hydrosulfonate, formed by citral + labil citral dihydrodisulfonate $C_9H_{16}CHO.SO_3Na$ (constitution not known). *labil.*

(5) Citral trihydrosulfonate.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\overset{(HX)}{C}-CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{\overset{(HX)}{C}}}-CH.CH\!<\!\!\begin{matrix} OH \\ OSO_2Na \end{matrix} \qquad \textit{labil.}$$

(6) A stable form of (5). *stable.*

The hydrogenation of citral is of considerable industrial interest on account of the availability of citral in oil of lemon grass and the possibility of its conversion into the more valuable rose like citronellol, or the hydrogenation of one double bond only, yielding citronellal which, as noted above, is quantitatively convertible into isopulegol and the latter substance being convertible by hydrogenation into the well-known article of commerce menthol, now derived entirely from oil of peppermint. Skita [194] found that on hydrogenating over nickel at 190°–200°, chiefly a decane was formed, and at a lower temperature, 140°, and under pressure Ipatiev showed that a decanol was the chief product. Law [195] attempted to reduce citral by electrolytic reduction in

[194] *Chem. Zentr.* *1911*, I, 1209.
[195] *J. Chem. Soc.* *101*, 1024 (1912).

alcohol acidified by sulfuric acid, but he was evidently not familiar with the properties of citral and related substances and it is impossible to tell from his article just what the result was.[196] According to Paal [197] hydrogenation by colloidal paladium or platinum, or by catalytic masses consisting of a supporting material on which small proportions of one of these metals are deposited, converts citral first to inactive citronellal and then to the saturated aldehyde tetrahydrocitral; geraniol is reduced to inactive citronellol and the saturated alcohol tetrahydrogeraniol. (This alcohol has recently been further studied by Ishizaka, *Ber. 41,* 2483 (1914), who also prepared it by Paal's method.) Skita states that citral yields both citronellal and citronellol together with a dimolecular aldehyde $C_{20}H_{34}O_2$ when using colloidal palladium as a catalyst.

Condensation of aliphatic aldehydes with β-naphthylamine and pyruvic acid usually yields well crystalline products suitable for the purpose of identification. Citral condenses with these two substances to form citryl-β-naphthocinchoninic acid, melting at 199°–200°. Citral oxime and the phenylhydrazone are liquid at ordinary temperatures. Cyanacetic and malonic acid condense readily yielding well crystalline products.

$$C_9H_{15}CHO + H_2C{<}\begin{matrix}CN\\CO_2H\end{matrix} \longrightarrow C_9H_{15}CH = C{<}\begin{matrix}CN\\CO_2H\end{matrix}$$

$$C_9H_{15}CHO + H_2C{<}\begin{matrix}CO_2H.\\CO_2H\end{matrix} \longrightarrow C_9H_{15}CH = C{<}\begin{matrix}CO_2H\\CO_2H\end{matrix}$$

Citral also condenses readily with acetone in the presence of alkalies, and this led Tiemann [198] to the discovery of the ionones. The formation of *pseudo*-ionone is an example of the well-known type of condensation illustrated by the formation of croton aldehyde, and mesityl oxide. According to Tiemann's patent specifications the condensation is effected by means of barium hydroxide, but other condensing agents give better results, for example 5 per cent of sodium ethoxide in absolute alcohol.[199] The resulting mixture is distilled and the fraction boiling at 138°–155° at 12 mm. is purified from unchanged citral and condensation products formed from acetone alone, by distilling with

[196] In the opinion of the writer, Law's experiments are of considerable interest and would be worth repeating with the coöperation of a skilled organic chemist.
[197] U. S. Pat. 1,210,681; *Chem. Abs.* 8, 1019 (1917).
[198] *Ber.* 26, 2675 (1893).
[199] Slack, *Pref. & Ess. Oil Record.* 7, 389 (1916).

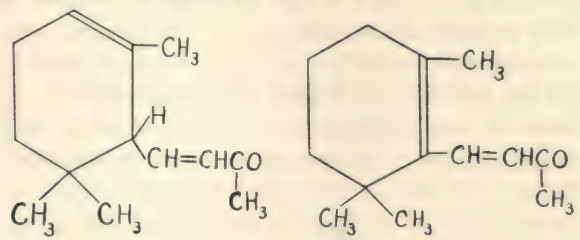
steam, these impurities being easily volatile. By a second vacuum distillation of this product a very pure pseudo-ionone boiling at 143°–145° is obtained.

$$\begin{array}{l} \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! C = CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CH.CHO + H_3C - CO - CH_3 \longrightarrow \\[2ex] \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!>\! C = CH.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}} = CH.CH = CH.COCH_3 \end{array}$$

pseudo-ionone.

The physical properties of pseudo-ionone are as follows; specific gravity at 20° = 0.8980, refractive index$_D$ = 1.53346, boiling-point at 12 mm. = 143°–145°

When pseudo-ionone is heated with dilute sulfuric acid, about 1 per cent, for several hours, ring closing results, probably through the intermediate addition of water and subsequent decomposition, giving two isomeric ionones, designated as α and β.



α-ionone β-ionone

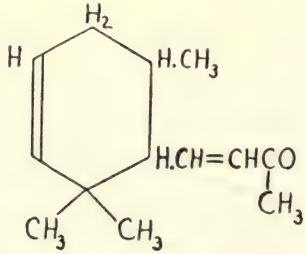
The odors of the two isomers are noticeably different, α-ionone having a sweeter odor more nearly resembling orris root and β-ionone, in very dilute solutions, about 1 : 10,000, resembling more closely the fresh wood violet. Commercial ionone is usually a mixture of the two isomers containing mostly α-ionone. The conditions under which pseudo-ionone is condensed affect the relative proportions of α and β-isomers, more concentrated sulfuric acid at low temperatures increasing the proportion of β-ionone while phosphoric, hydrobromic and hydrochloric acid yield chiefly α-ionone. Many methods have been proposed to separate the two isomers, of which two only will be mentioned. Pure α-ionone was isolated by Tiemann by making the oxime

of a commercial ionone containing mostly α-ionone, recrystallizing the oxime from petroleum ether and regenerating the ketone by means of dilute sulfuric acid. One method of separation is based upon the insolubility of the sodium hydrosulfonate of α-ionone in aqueous sodium chloride solutions.[200] If sodium chloride is added to a hot solution of the sodium hydrosulfonates, the α-ionone derivative separates, crystallizing in very small plates; the β-ionone hydrosulfonate remains in solution. Gildemeister [201] notes the following physical properties for commercial ionone; boiling-point 104°–109° (4 to 5 mm.), $d^{15°}$ 0.9350 to 0.9403, $n\frac{20°}{D}$ 1.5033 to 1.5051. Chuit [202] gives the following for the two isomers.

	α-Ionone	*β-Ionone*
Boiling-point	127.6° (12mm.)	134.6° (12mm.)
Density, 15°	0.9338	0.9488
Refractive index	1.50001	1.52008
p-Bromophenylhydrazone, M. P.	142°–143°	116°–118°
Semicarbazone	107°–108°	148°–149°

The ionones may be hydrogenated to the ketone tetrahydroionone by means of hydrogen and colloidal palladium [203] or the ketone group may be converted to $>CH_2$ without affecting the double bonds.[204]

Irone: On account of its similarity to the ionones, this ketone, an isomer of the synthetic violet ketones, may be mentioned here. It was isolated from the volatile oil of orris root and studied by Tiemann. It has been made by the condensation of Δ^4 cyclocitral and acetone,[205] and its close similarity to the ionones is shown by the following structure.

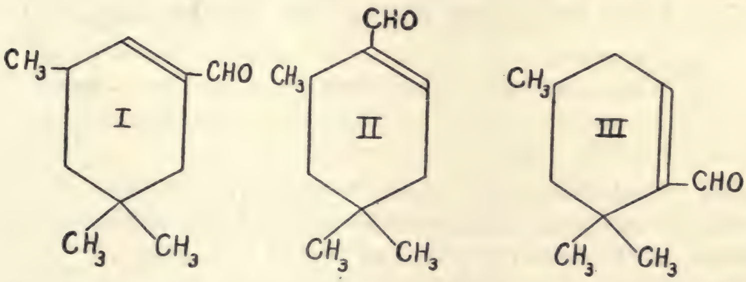


The physical properties of irone are, boiling-point 144° (16 mm), $d^{15°}$ 0.9391, $n\frac{20°}{D}$ 1.5017. Its characteristic derivatives are the oxime,

[200] *Chuit, Rev. Gen. Chim. 6*, 432 (1903).
[201] *"Die Aetherischen Oele"*, Vol. I, 485. Ed. II (1910).
[202] *Loc. cit.*
[203] Skita, *Ber. 45*, 3312 (1912).
[204] Kishner, *J. Russ. Phys.-Chem. Soc. 43*, 1398 (1912).
[205] Merling & Welde, *Ann. 366*, 119 (1909).

melting point 121.5°, p-bromophenylhydrazone melting at 174°–175° and thiosemicarbazone melting at 181°. Irone is not made synthetically on an industrial scale, nor isolated as such from the volatile oil of violet root, or orris.

In view of the commercial value of the ionones Merling and Welde[206] undertook a study of similarly constituted unsaturated ketones. Any slight change in the constitution of these ketones causes considerable difference in odor. While the group $-CH=CH-CO-CH_3$ is essential to odors of this kind, as is shown by the fact that on hydrogenating the double bonds, the fragrance of the ionones disappears, the particular quality of the odor is influenced greatly by the relative positions of the other ethylene bond and the methyl groups. Condensation products with acetone were prepared from the following three aldehydes, isomeric with cyclocitral.



The product derived from I was almost odorless but the products from II and III had faint violet like odors. The most intense odor is obtained when the aldehyde group is situated between the methyl and dimethyl groups. The perfume character of such acetone condensation products disappears when the aldehyde group does not adjoin a methyl group. Nevertheless the grouping

$$\begin{array}{ccccc} & CH_3 & & & \\ & | & & & \\ - & C & - CH - & C< & \\ & | & | & | & \\ & CH_3 & CHO & CH_3 & \end{array}$$

does not yield a perfume when condensed with acetone, as is shown by the condensation product obtained from β-isopropylbutaldehyde and acetone, but when these groups are present in the cyclogeraniolene ring, a perfume results. The importance of the tertiary butyl group $-C(CH_3)_3$, to the odor of musk, has been brought out by the work

[206] *Ann.* 366, 119 (1909).

of Bauer on artificial musk.[207] Austerweil [208] has shown that the group $>C=CH.\underset{\substack{|\\ OH}}{C}RR_1$ appears to be necessary to produce geraniol like odors.

The condensation of citral with ethyl acetoacetate has been studied by Knoevenagel [209] who isolated five isomeric ethylcitrylidene acetol acetates. Condensation is brought about by adding a very small quantity of piperidine to a mixture of ethyl acetoacetate and citral at — 15° and allowing to stand two days. The structure of these condensation products is not yet definitely known.

Citral reacts normally with methyl or ethyl-magnesium bromide to give secondary alcohols of rose like odor.[210]

Sesquicitronellene, $C_{15}H_{24}$. This so-called aliphatic sesquiterpene was discovered in Java citronella oil by Semmler and Spornitz.[211] It has four double bonds, three of which are probably conjugated.

Mol. Ref.	74.53
Mol. Ref. calc. for $C_{15}H_{24}$ /= 4	69.6
E M—	4.9

Sodium and alcohol readily reduce it to $C_{15}H_{26}$ (evidence of at least one pair of conjugated double bonds) and hydrogen in the presence of platinum black yields the saturated acyclic hydrocarbon $C_{15}H_{32}$. As is frequently observed among the sesquiterpenes ring closing is easily effected, being brought about in this case by concentrated formic acid. Sodium and alcohol do not reduce the cyclic hydrocarbon showing that ring formation has occurred through one of the conjugated double bonds. The original sesquicitronellene is readily oxidized and polymerized. Its physical properties are, boiling-point 138°–140° (9 mm.), d_{20} 0.8489, n_D 1.53252.

Spinacene. $C_{30}H_{50}$. This very remarkable unsaturated hydrocarbon has recently been described by Chapman [212] and by Tsujimoto.[213] It has been found in the livers of several species of the Spinacidae, a family of the Selachoidei, or sharks, and Chapman has therefore named it spinacene. In the fresh liver oils of certain species this hydrocarbon

[207] *Ber.* *24*, 2832 (1891); *32*, 3647 (1899).
[208] *Compt. rend.* *151*, 440 (1910).
[209] *J. prakt. chem.* (2), *97*, 288 (1918).
[210] Bayer & Co., *Chem. Zentr.* *1904*, II, 624, 1269.
[211] *Ber.* *46*, 4025 (1913).
[212] *J. Chem. Soc.* *111*, 56 (1917); *113*, 458 (1918).
[213] *Chem. Abs.* *12*, 1004 (1918).

constitutes about 90 per cent of the oil. Fish liver oils previously known, such as those of the haddock, skate, hake, cod, and tunny, contain only about 2 per cent of unsaponifiable matter which appears to be cholesterol. From the standpoint of physiological chemistry, the manner of formation, secretion and physiological utilization of such an oil is of great interest, and inasmuch as the sharks are found, fossilized, in many strata, geologically very old, the probability that shark liver oils have contributed to the formation of petroleum is at once suggested.

Chemically, spinacene is of more than ordinary interest. Dry hydrogen chloride passed into a cooled ether solution of spinacene forms the crystalline hexahydrochloride, $C_{30}H_{50}.6HCl$, and bromine in dry ether yields the crystalline dodecabromide $C_{30}H_{50}Br_{12}$. Like chlorine and bromine derivatives of petroleum hydrocarbons and the terpenes, these spinacene derivatives are unstable and readily decompose on heating. The hydrocarbon accordingly contains *six* double bonds. A moderately stable crystalline trinitrosochloride can be prepared by the usual methods. By catalytic hydrogenaton by means of platinum black, Chapman obtained the saturated hydrocarbon $C_{30}H_{62}$, which is liquid at — 20° and therefore is not a normal paraffine. Exaltation of the refractive index and partial polymerization by metallic sodium indicate that probably two pairs of double bonds are in conjugated positions. On distilling over sodium, partial decomposition also occurs, forming a hydrocarbon $C_{10}H_{18}$, which appears to be a monocyclic hydrocarbon containing one double bond, boiling at 170°–175°, and much resembling cyclodihydromyrcene in its properties.

Cholesterylene: The hydrocarbons resulting from the decomposition of cholesterol or cholesteryl chloride have been repeatedly investigated on account of the possible connection of this hydrocarbon with the optical activity of petroleum. The properties of "cholesterylene" vary considerably according to its method of preparation. When equal parts of cholesterol and infusorial earth are rapidly heated to 280°–300° a solid cholesterylene is obtained, which is capable of adding four atoms of hydrogen to form the solid cholestane. A similar mixture slowly heated for about eight hours at 300° gives an oil, probably a mixture, boiling at 257°–267° at 12 mm., D = 0.9572 and $[\alpha]_D + 49.12°$. The product obtained by rapid heating is laevo rotatory.[214] Cholesteryl chloride [215] yields an oil having properties practically identical with those noted above.

[214] Steinkopf, *J. prakt. chem.* (2) *100*, 65 (1919).
[215] Mauthuer & Suida, *J. Chem. Soc. Abs.* *1904*, I, 49; *1909*, I, 714.

ACYCLIC UNSATURATED HYDROCARBONS OF KNOWN CONSTITUTION, C_6 TO C_{16}.

	Name	*Boiling-Point*	*Density*		*Remarks: Characteristic Derivatives*	*References**
C_6H_{12}	Hexene-(1)	60.5°– 61.5°	0.6830	$\left(\frac{20°}{20°}\right)$		1–2
"	2-Methylpentene(2)	65. °– 67. °	0.687	(19°)	Adds HI to give a hexyl iodide B.-P. 142°	3
"	2-Methylpentene-(3)	58. °– 59. °	0.6695	$\left(\frac{20°}{0°}\right)$		4
"	3-Methylpentene-(2)	69.5°– 71. °	0.698	(19°)	From 2-iodo-3-methylpentane by Zn in acetic acid	5
"	3.3-Dimethylbutene-(1)	41.2°	0.6549	$\left(\frac{18°}{4°}\right)$		6
"	2-2-Dimethylbutene-(4)	40.9°– 42.3°	.....		Adds HBr to $(CH_3)_3C.CH_2CH_2Br$	7
"	2.3-Dimethylbutene-(1)	56. °– 59. °	0.6795	(0°)	Prep. by decomp. $(CH_3)_2C.(OH).CH(CH_3)_2$	8
"	2.3-Dimethylbutene-(2) (Tetramethylethylene)	72. °– 73. °	0.7280	(0°)	Prep. from $(CH_3)_2CBr.CH(CH_3)_2$	8 & 9
C_7H_{14}	Heptene-(1) ?	95. ° 97. °– 99. °	0.6999	$\left(\frac{15°}{4°}\right)$	By decomp. n.heptylpalmitate at 350°	10 & 11
C_7H_{14}	Heptane-(2) ?	98.5°	.....		As a mixture, by decomp. of chlorinated heptane	12
"	5-Methylhexene-(1)	85. °– 86. °	0.7160	$\left(\frac{15°}{15°}\right)$		2
"	4-Methylhexene-(4) ?	85. °– 90. °	0.7301	$\left(\frac{25°}{4°}\right)$		13
"	3-Ethylpentene-(2)	97. °– 98. °	0.72544	$\left(\frac{15°}{4°}\right)$	By decomp. triethylcarbinol	14
"	2.3-Dimethylpentene-(2)	92. °– 95. °	0.7355	(0°)		15
"	2.4-Dimethylpentene-(2)	83. °– 84. °	0.7144	(0°)	By KOH on iodide of dimethylisobutyl-carbinol	16
"	2.2.3-Trimethylbutene-(3)	78. °– 80. °	.....		From pentamethylethyl iodide + KOH	17
C_8H_{16}	Octene-(1) ?	122. °–123. °	0.7217	(17°)		18

* See reference on page 209.

	Name	Boiling-Point	Density	Remarks: Characteristic Derivatives	References*
C_8H_{16}	Octene-(1) and -(2) ?	122.5°–123.5°	0.7226 $\left(\frac{0°}{4°}\right)$; 0.7197 $\left(\frac{20°}{4°}\right)$	By decomp. methylhexylcarbinol	19
"	6-Methylheptene-(1)	111. °–112. °	0.7124 $\left(\frac{20°}{4°}\right)$	From iso-amyl-magnesium bromide and allyl bromide	2
"	2-Methylheptene-(2)	123. °–125. °	0.816 $\left(\frac{20°}{4°}\right)$		20
"	2-Methylheptene-(3)	120.4°	0.7314 $\left(\frac{20°}{4°}\right)$		21
"	4-Methylheptene-(4) ?	115. °–120. °	0.7411 $\left(\frac{25°}{4°}\right)$		13
"	3-Ethylhexene	119.4°	0.7364 $\left(\frac{20°}{0°}\right)$		21
"	2-Methyl-3-ethylpentene-(2)	114.5° to 116.5°	.....		22
C_9H_{18}	Nonene-(2) ?	147. °–148. °	.....	By heating methylheptylcarbinol with 60% sulfuric acid	23
"	2 Methyloctene-(1)	141.5°–143. °	.....		24
"	4-Methyloctene-(4) ?	133. °–138. °	0.7388 $\left(\frac{25°}{4°}\right)$		25
$C_{10}H_{20}$	-Decene-(1) ?	172. °	0.7630 (0°)	By heating Ba undecylenate + Na ethylate	26
"	2.7-Dimethyloctene-(2)	159. °–162. °	0.7475 $\left(\frac{20°}{0°}\right)$		27
"	3.7-Dimethyloctene-(2)	162. °–163. °	0.7490 $\left(\frac{20°}{0°}\right)$	Synthesized from methylheptanone	28
"	2.6-Dimethyloctene-(2) ?		0.7533 $\left(\frac{20°}{0°}\right)$		29

* See reference on page 209.

Name		*Boiling-Point*	*Density*	*Remarks: Characteristic Derivatives*	*References**
$C_{10}H_{20}$	2.6-Dimethyloctene ?	162. °	0.7558– $\left(\frac{20°}{4°}\right)$		30
"	4.7-Dimethyloctene-(4) ?	152. °–157. °	0.7460– $\left(\frac{25°}{4°}\right)$		31
"	2-Methyl-5-ethylheptene-(5)	157. °–158. °	0.7609 (0°)		32
"	3.3.5-trimethylheptene-(4)	157. °–157.5°	0.7878 (0°)		33
$C_{11}H_{22}$	-Undecene-(1) ?	84. °(18mm.)	.....	From methylnonylcarbinol	34
"	-Undecene-(2)	191. °–193. °	0.7735– $\left(\frac{15°}{15°}\right)$	From methylnonylcarbinol	34–35
"	4.8-Dimethylnonene-(4)	165. °–169. °	0.75301– $\left(\frac{25°}{4°}\right)$		36
$C_{12}H_{24}$	Dodecene-(1)	96. °(15mm.)	0.7732– $\left(\frac{0°}{4°}\right)$	By distillation of dodecylpalmitate	37
"	2.5.8-Trimethylnonene-(4)	74. °(9mm.)	0.7768 (0°)	From methyl di-isoamylcarbinol	38
"	2.5-Dimethyl-4-isobutylhexene-(4)	65. °(10mm.)			39
$C_{14}H_{28}$	Tetradecene-(1) ?	127. °(15mm.)	0.7852– $\left(\frac{0°}{4°}\right)$	From the palmitic ester	37
$C_{16}H_{28}$	Hexadecene-(1) ?	274. °			
	(Cetene)	155. °(15mm.)	0.7842 $\left(\frac{0°}{4°}\right)$	From the palmitic ester	37–38

* See reference on page 209.

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Chapter VI. Polymerization of Hydrocarbons.

The polymerization of unsaturated hydrocarbons is a phenomenon the mechanism of which is exceedingly obscure, in fact, no very plausible theories have been advanced to explain this kind of condensation, although the process is accepted and utilized daily in the industries. When unsaturated petroleum hydrocarbons are polymerized by sulfuric acid it has been assumed that alkyl sulfuric acid esters are formed which may then condense with other molecules of the original olefine, with the liberation of sulfuric acid,[1]

$$(1)\qquad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH_2+H_2SO_4 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\underset{OSO_3H}{|}}{C}\!-\!-CH_3$$

$$(2)\qquad \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\underset{OSO_3H}{|}}{C}\!-\!-CH_3+\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH_2 \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH.\underset{\underset{CH_3}{|}}{C}\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

However, polymerization of hydrocarbons is brought about by a great variety of substances, energetic reagents such as anhydrous aluminum chloride or bromide, zinc chloride, ferric chloride, sulfur chloride, and also such substances as fuller's earth, forms of energy such as light, heat, the silent electric discharge and also certain metals, for example, metallic sodium. It is quite probable, therefore, that we shall have to go much deeper than the drawing of graphic formulæ for plausible theories of polymerization; in fact, the question really is one involving the nature of valence. It is beyond the scope and purpose of the present volume to go far afield in reviewing the subject of valence, but there are a number of phenomena, such as polymerization and the mechanism of organic reactions, absorption of light and its alteration as in fluorescence, and the decomposition of substances under the influence of heat which are undoubtedly very closely related and, with

[1] **Kondakow, *J. prakt. chem.* 54, 442 (1896).**

valence, belong fundamentally to the subject of the constitution of matter. The observations noted in the following discussion have been brought together on account of their interest to organic chemists, rather than for any light that may be thrown upon the mechanism of polymerization.

Ethylene, as noted elsewhere in these pages, is relatively stable, but, at temperatures within the range 400°–450°, condensation, in contact with iron or copper, is fairly rapid.[2] Many substituted ethylenes containing negative groups such as chlorine, or the phenyl group, polymerize on standing at room temperature, for example, styrene $C_6H_5CH = CH_2$, vinyl chloride $CH_2 = CHCl$ (polymerization is particularly rapid in sunlight), 1, 1-dichloroethylene $CH_2 = C.Cl_2$, vinyl bromide in sunlight, 1-chloro-1-bromoethylene $CH_2 = C.ClBr$, and 1, 1-dibromoethylene $CH_2 = CBr_2$. These substances are rapidly oxidized by air or oxygen. On the other hand, allyl chloride and bromide, $CH_2 = CH.CH_2X$, trichloroethylene $CHCl = CCl_2$, and 1.2 dibromoethylene, $CHBr = CHBr$ are not spontaneously polymerized and are not appreciably oxidized on standing in contact with air or oxygen.

Vinyl bromide, $CH_2 = CHBr$, is polymerized on standing in sunlight to what Ostromuislenski[3] calls α-caouprene bromide. Polymerization under these conditions is very greatly affected by other substances, light low boiling hydrocarbons very greatly retarding the reaction. This polymer, α-caouprene bromide, dissolves very readily in carbon bisulfide and its chemical properties are of particular interest, for example, it is quite inert to inergetic oxidizing agents and to concentrated mineral acids. Under the influence of ultraviolet light the polymerization appears to proceed further, forming what have been named β- and γ-caouprene bromides. The β-caouprene bromide is soluble in carbon bisulfide but the γ-product is quite insoluble but swells in this solvent. The γ-product may be converted into the soluble β-bromide by boiling with chlorobenzene and then precipitating with petroleum ether. The tetrabromide of butadiene-caoutchouc, described by Harries, also exists in three forms whose behavior is apparently identical with the polymerized vinyl bromides just described. Ostromuislenski regards the polymers of vinyl bromide as structurally arranged as follows,

$$\ldots\ CH_2CHBr.CH_2CHBr.CH_2CHBr\ \ldots\ldots\ldots\ldots$$

[2] Ipatiev, *J. Chem. Soc. Abs.* *1907*, I, 5.
[3] *J. Russ. Phys.-Chem. Soc.* *44*, 204 (1912).

Butylene, amylenes and hexylenes are more easily polymerized than their higher homologues and when condensation of such mono-olefines occurs, ring formation does not take place.

Hydrocarbons containing two or more conjugated ethylene bonds are more rapidly oxidized by oxygen and are very easily polymerized, as, for example, butadiene (also called erythrene and divinyl) isoprene, dimethylallene, piperylene, the so-called aliphatic terpenes, myrcene ocimene, cyclopentadiene and the fulvenes, cyclohexadiene and the like. The structure of the polymers of these substances is known in but few instances, but one instance of ring formation is well known, i. e., the condensation of isoprene to the cyclohexene derivative dipentene. Also, dimethyl and tetramethylallene yield *cyclobutane* derivatives on polymerization.

Dimethylallene, $(CH_3)_2C = C = CH_2$, is of iterest as an isomer of isoprene. This hydrocarbon may readily be converted to isopropyl acetylene, and *vice versa,* indicating that the internal stress in the two hydrocarbons is approximately of the same order,

$$(CH_3)_2C = C = CH_2 \leftrightarrows (CH_3)_2CH - C \equiv CH.$$

Tetramethylallene is also easily changed to an acetylene derivative. In the series beginning with allene and including methyl, dimethyl, trimethyl and tetramethylallene, the stability *diminishes* with increasing substitution of methyl groups.[4]

When dimethylallene condenses to the dimeric cyclobutane derivative six isomeric hydrocarbons are possible but two have been isolated, i. e.,

$$\begin{array}{l} CH_2 - C = C(CH_3)_2 \\ | \qquad\; | \\ CH_2 - C = C(CH_3)_2 \end{array} \quad \text{boiling-point } 61°\text{–}62°, \text{ 9 mm.}$$

$$\begin{array}{l} CH_2 = C - C(CH_3)_2 \\ \qquad\;\; | \quad\;\, | \\ (CH_3)_2C - C = CH_2 \end{array} \quad \text{boiling-point } 37°\text{–}38°, \text{ 9 mm.}$$

Tetramethylallene condenses to the hydrocarbon.[5]

[4] Mereshkowski, *J. Russ. Phys.-chem. Soc.* 45, 1940 (1913). Tetramethylallene was obtained pure for the first time by Mereshkowski, by treating $(CH_3)_2C{=}\underset{\displaystyle Br}{\underset{|}{C}}{-}CH(CH_3)_2$ with alcoholic caustic potash in an autoclave at 130°, illustrating the marked effect of the double bond on the reactivity of the bromine atom.

[5] This hydrocarbon has the unusually high optical exaltation of 2.596, due doubtless to *conjugated* linkings of *semi-cyclic* character and also perhaps to the presence of the cyclobutane ring.

$$\left.\begin{array}{l} (CH_3)_2C = C = C(CH_3)_2 \\ \\ (CH_3)_2C = C = C(CH_3)_2 \end{array}\right\} \longrightarrow \begin{array}{l} (CH_3)_2C - C = C(CH_3)_2 \\ \qquad\quad\;\, | \qquad | \\ (CH_3)_2C - C = C(CH_3)_2 \end{array}$$

Polymerization is a property which is probably common to all substances containing ethylene linkings.[6]

In a study of the polymerization of α, β unsaturated ketones, Ruzicka [*Helv. chim. Acta, 3,* 781 (1920)] showed that the point of attack was the ethylene bonds, not the CO groups.

Conjugated Dienes and the Synthesis of Rubber.

The preparation of conjugated dienes has become a matter of great interest on account of the property, which some of these unsaturated hydrocarbons possess of polymerizing to rubber-like substances. Many industrially important organic substances derived from natural sources can also be manufactured by synthetic methods but the competition

[6] Ethylene bonds undoubtedly play a very essential part in the polymerization of fatty oils, and the phenomenon is most pronounced in the case of highly unsaturated oils such as tung, linseed, walnut and certain fish oils. However, the glycerine and carboxyl groups also probably enter into the process of condensation. Kronstein (*Ber. 49,* 722 [1916] showed that olive and cottonseed oils contain considerable proportions of glycerides which gelatinize like tung oil if the non-polymerizing portions of these oils are first removed by distillation. Polymerization of these oils is accompanied by a decrease in their iodine absorption values. Depolymerization takes place readily since Morell (*J. Soc. Chem. Ind. 37,* 181 [1918]) has shown that the methyl esters, derived from polymerized tung oil, are of normal molecular weight. Salway (*J. Soc. Chem. Ind. 39,* 324T, [1920]) shows that the introduction of free fatty acids accelerates the polymerization of such oils (whale oil), and when the free fatty acids are heated, decrease of the iodine value and refractive index occurs. When the natural glycerides are heated, Salway supposes, (1) splitting off of free fatty acid; (2) condensation of the free fatty acid with the unsaturated linkings of the fatty oil; (3) possible anhydride formation in which reaction the free alcoholic glyceryl radicles take part.

(1)

$$\begin{array}{l} CH_2O.OCR \\ | \\ CH_2O.OCR \\ | \\ CH_2O.OC(CH_2)_4CH{=}CH.C_{11}H_{19} \end{array} \longrightarrow \begin{array}{l} CH_2OH. \\ | \\ CH_2O.OCR. \\ | \\ CH_2O.OC(CH_2)_4CH{=}CH.C_{11}H_{19} \end{array} + \quad RCO.OH.$$

(2)

$$\longrightarrow \begin{array}{l} CH_2OH. \\ | \\ CH_2O.OCR \\ | \\ CH_2O.OC.(CH_2)_4CH{-}CH_2.C_{11}H_{19} \\ \qquad\qquad\qquad\qquad\;\; | \\ \qquad\qquad\qquad\qquad\; O.OCR \end{array} \longrightarrow \begin{array}{lcl} CH_2 & {-}O{-} & CH_2 \\ | & & | \\ C\ldots. & & C\ldots. \\ | & & | \\ C\ldots. & & C\ldots. \end{array}$$

anhydride formation

of the two methods is often very close, and while the future of synthetic rubber is a matter of opinion, all chemists interested in this problem should keep in mind the fact that plantation rubber from *Hevea braziliensis* can be produced at a cost of approximately twenty-five cents per pound. The present relative importance of synthetic and natural rubber is not a matter of opinion, but of record, and with the exception of a quantity produced in Germany during the war, no synthetic rubber has been produced on an industrial scale or at prices which threaten the rubber plantations. The production of rubber from *Hevea* plantations has been much greater than the pioneers of the industry had anticipated on account of the "wound response" of the trees on tapping.[7] The synthesis of good gutta percha would seem to offer a better chance of commercial success on account of the slow growth of the trees yielding gutta and the apparent difficulties of solving this phase of the rubber business by plantation methods. Yet even in this case the struggle between synthetic and natural camphor is suggestive. Camphor trees are seldom felled for camphor distillation until they have reached the age of approximately fifty years, yet camphor plantations, distilling the leaves and twigs, have been undertaken on an extensive scale and the cost of manufacturing synthetic camphor has increased with the higher cost and diminishing supply of turpentine, the necessary raw material.

The history of the subject[8] of artificial rubber has been marred by polemical controversies which have arisen largely on account of definitions and the difficulty of determining just what rubber is structurally and the difficulty of proving the identity of such amorphous substances. As regards the question of the identity of polymerized isoprene rubber and natural Hevea rubber, it now appears that the former, when made either by polymerization by metallic sodium or by peroxides, is not homogenous, as is indicated by the fact that the ozonides yield succinic acid, acetonylacetone, laevulinic aldehyde and laevulinic acid, corresponding to the two dimeric isoprene complexes 1.5-dimethyl-$\Delta^{1.5}$-cyclo-octadiene and 1.6-dimethyl-$\Delta^{1.5}$-cyclo-octadiene.[9] Natural *Hevea* rubber, on the other hand, appears to be a homogenous product, the ozonide decomposition products being referrable to the

[7] Parkin, Rubber Cultivation in the Far East, *Science Progress.* I. Jan. 1910; II. April, 1910. According to Eaton, *Chem. Trade J. 1921,* 242 approximately 2,000,000 acres are under cultivation for rubber.

[8] Cf. Pond, *J. Am. Chem. Soc. 36,* 165 (1914); Luff, *J. Soc. Chem. Ind. 35,* 983 (1916); Perkin, *J. Soc. Chem. Ind. 31,* 616 (1912); Gottlob, *Indiana Rubber J. 58,* 305, 348, 391, 433 (1919).

[9] Steimmig, *Ber. 47,* 350 (1914).

1.5-dimethyl-$\Delta^{1\cdot 5}$-cyclo-octadiene complex. The first direct evidence obtained by Harries of an eight carbon ring complex was later shown to be incorrect, the ketone then considered to be cyclo-octane-1.5-dione proving to be impure heptane-2.6-dione.[10] For practical purposes, however, Ostromuislenski is little concerned with chemical standards of comparison between natural rubber and synthetic colloids resembling them, and advocates [11] a classification based upon the temperatures at which the colloid acquires and loses its elastic properties, and the range between these temperature limits. When these agree closely with the values for natural caoutchouc he proposes that the colloid be classed as normal, regardless of its ozonide decomposition products. Considering the conflicting results of different experimenters with the ozone method, and the difficulties of such work, the proposed classification would probably be as consistent and also more useful.

Harries has contended that the earlier investigators, who discovered the polymerization of isoprene, did not really produce caoutchouc, but the question seems a futile and purposeless one. That isoprene could be polymerized to an amorphous *rubber-like* substance was evident from the early work of Greville Williams [12] who did not recognize his product as rubber, but whose description of the product, together with the results of later repetition of his work, indicate that his product was in fact rubber, and Bouchardat [13] who, in 1875, treated isoprene with concentrated hydrochloric acid at 0°, and Tilden [14] who obtained a similar product in 1882 and announced later, 1892, that isoprene polymerizes spontaneously on long standing in the light and in contact with air.[15] Wallach [16] showed that light causes the polymerization of isoprene in a sealed tube, but the change is more rapid in contact with oxygen or air. The polymerization of isoprene and similar dienes is more fully discussed in a separate section on the properties of unsaturated hydrocarbons.

As regards the preparation of the dienes, it is possible to note processes which are of industrial promise and, processes which are not likely to become commercial on account of the cost of raw materials or operating difficulties, or both.

[10] Harries, *Ber.* *47*, 784 (1914).
[11] Cf. *J. Russ. Phys.-Chem. Soc.* *47*, 1928 (1915).
[12] *Phil Trans.* *150*, 254 (1860).
[13] *Compt. rend.* *89*, 361, 1117 (1879).
[14] *Chem. News.* *46*, 220 (1882).
[15] *Chem. News*, *65*, 265 (1892).
[16] *Ann.* *227*, 295 (1885).

The earlier workers prepared isoprene by the destructive distillation of rubber, a typical distillation yielding the following products:

Isoprene	6.2 per cent
Dipentene	46.0 " "
Higher boiling oils	43.8 " "
Carbonized residue	1.9 " "
Loss and mineral matter	1.9 " "

The formation of isoprene by pyrolysis of turpentine was first noted by Hlasiwetz [17] who passed turpentine through a "red-hot" iron tube packed with broken porcelain. A large number of products were obtained and isoprene was not then actually identified in the low boiling fraction, but Tilden [18] later repeated this work and proved the formation of isoprene in this manner. The yields of isoprene obtained by the pyrolysis of turpentine and dipentene vary greatly and are generally very low. Harries [19] obtained 10 per cent of isoprene by decomposing commercial pinene by means of his isoprene lamp (wires heated electrically to low red heat). Herty and Graham [20] reported yields of 5.5 to 8 per cent from turpentine fractions, and 12 per cent from limonene while Harries obtained yields of 30 to 50 per cent from the latter hydrocarbon. By decomposing under reduced pressure, 4 mm., yields as high as 60 per cent are said to be possible from limonene.[21] Schorger and Sayre [22] also report low yields from turpentine, the two pinenes, α and β, giving substantially the same yields. Very little attention has been paid to the temperature required for optimum yields of isoprene but, in contact with glass or porcelain, this temperature appears to be 550° to 600°.[23] According to Ipatiev, the condensation of isoprene to dipentene is fairly rapid at 300°.

Small yields of butadiene and isoprene can also be obtained by the pyrolysis of petroleum oils and have been identified in the low boiling fractions of the light oils obtained by compressing oil gas or Pintsch gas to 150 to 200 pounds pressure. However, the fact that they have been detected in these pyrolytic products is a tribute to the analytical skill of the chemists who investigated these hydrocarbon mixtures.[24] Nevertheless, the preparation of isoprene and butadiene by the pyroly-

[17] *Ber. 9,* 1991 (1876).
[18] *J. Chem. Soc. 45,* 410 (1884).
[19] *Ann. 383,* 228 (1911).
[20] *J. Ind. & Eng. Chem. 6,* 803 (1914).
[21] Staudinger & Klever, *Ber. 44,* 2212 (1911).
[22] *J. Ind. & Eng. Chem. 11,* 924 (1915).
[23] Mahood, *J. Ind. & Eng. Chem. 12,* 1152 (1920); Heinemann, Brit. Pat. 14,040; 24,236 (1910); 1953 (1912); Stephen, U. S. Pat. 1,057,680; Ostromuislenski, French Pat. 442,980 (1912); Schering, German Pat. 260,934 (1913).
[24] Armstrong & Miller, *J. Chem. Soc. 49,* 74 (1886).

sis of petroleum oils at about 700°, particularly *in vacuo*,[25] has recently been patented. This method presumably would give better results with light petroleum oils containing cyclohexane, cyclopentane, and their simpler homologues, since it has been claimed that tetrahydrobenzene yields a certain proportion of butadiene on decomposition under these conditions.[26] However, in the ten years which have elapsed since this work was done, there have been no industrial developments along this line and considering the small yield of the desired dienes, the value of petroleum oils for other uses, and the difficulty of purifying the desired hydrocarbons, it is very doubtful indeed if the direct pyrolysis of hydrocarbons will ever prove to be an economic method of producing these hydrocarbons. In this connection, it should be noted that Ostromuislenski [27] has shown that on polymerizing isoprene containing amylene or similar olefines, the resulting "rubber" is very sticky and soft.

Petroleum pentane is mostly normal pentane but attempts have been made to utilize this hydrocarbon as a raw material for the manufacture of isoprene. It may be said of all the chemical methods for the preparation of these unsaturated hydrocarbons that no really new methods or reactions have been developed; all of the known methods of producing unsaturated hydrocarbons have been applied to the preparation of these dienes but the great majority involve the elimination of halogens, usually chlorine, or of hydroxyl groups in the form of water. The production of isoprene from normal pentane involves the change to the carbon structure of *isopentane*. This is accomplished by one patentee [28] by taking advantage of the isomerization of olefines effected by heat, which has already been noted in the case of the butylenes. Thus pentane is chlorinated to a mixture of the monochlorides and these are converted to amylenes by pyrolysis in contact with barium chloride, lime or other methods, and the mixture of amylenes then passed over alumina at about 450°. Partial rearrangement to trimethylethylene occurs and on treating the resulting mixture of amylenes with hydrogen chloride this hydrocarbon reacts most readily, the chloride thus formed being separated by fractional distillation. The hydrocarbons thus separated are passed again over alumina at 450°, and so on. The purified monochloroisopentane is converted to trimethylethylene by the usual methods and this treated with chlorine to

[25] Engler and Staudinger, *Ber.* *46*, 2468 (1913); German Pat. 265,172 (1912).
[26] Farbenfabr, Elberfeld, German Pat. 241,895.
[27] *J. Russ. Phys.-Chem. Soc.* *48*, 1071 (1916); *Chem. Abs.* 11, 1768 (1917).
[28] Badische, German Pat. 280,596 (1919).

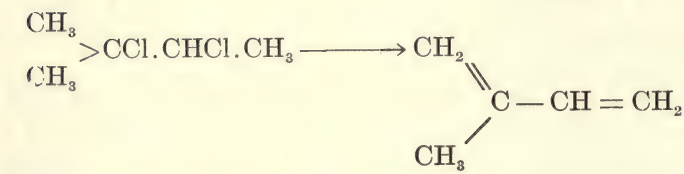
form the dichloride which then forms isoprene with the elimination of two molecules of hydrogen chloride. The reactions involved are as follows:

$$CH_3CH_2CH_2CH_2CH_3 \longrightarrow \text{monochlorides} \longrightarrow$$

$$\text{amylenes} \longrightarrow \left\{ \begin{array}{l} CH_3 \\ \quad\; >C=CHCH_3 \\ CH_3 \\ \quad \text{and isomers} \end{array} \right\} + HCl \longrightarrow$$

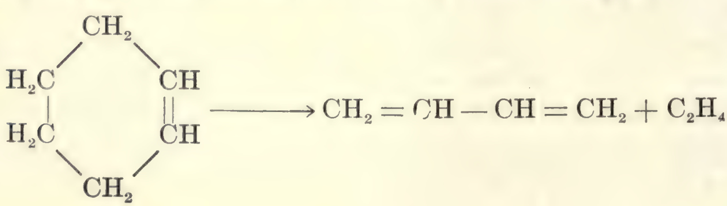
$$\begin{array}{l} CH_3 \\ \quad >CCl.CH_2CH_3 \\ CH_3 \end{array} \longrightarrow \begin{array}{l} CH_3 \\ \quad >C=CHCH_3 \\ CH_3 \end{array} \longrightarrow$$

(pure)



Petroleum pentane is one of the cheapest raw materials which have been suggested for this purpose but the process involves a large number of operations, distillations, purification of intermediates and the losses are large, for example, if each operation indicated above gave a yield of 90 per cent the final net yield of isoprene would be about 47 per cent. Pentane can, in fact, be chlorinated to monochloropentanes with a yield of about 90 per cent, exclusive of vaporization losses, but the losses on isomerizing the amylenes are large and it is impossible to chlorinate trimethylethylene without partially chlorinating further to trichlorides and tetrachlorides.

Several patented processes employ phenol and cresols as raw materials. Phenol may be hydrogenated to cyclohexanol, with good yields, and this alcohol may then be dehydrated by heating in contact with alumina, thoria or kaolin, to give cyclohexene. Cyclohexene gives small yields of butadiene and ethylene by direct pyrolysis,



Chlorination of cyclohexene to the dichloride, and then decomposing this, yields the conjugated diene, cyclohexadiene, but this hydrocarbon polymerizes to a substance more nearly resembling resin than rubber. Benzene itself is readily hydrogenated to cyclohexane and this may be converted to cyclohexene through the monochloro derivative by the usual methods [29] but none of these materials yield final products of good quality.

It is much easier to prepare isoprene and butadiene, and in much purer condition, by using butyl or isoamyl alcohol as the raw materials. A new method for the manufacture of n.butyl alcohol has been developed based upon the fermentation process of Fernbach,[30] the two principal products being n.butyl alcohol and acetone. Although originally developed in connection with the synthetic rubber problem it was carried out on a large scale during the recent war, essentially as a process for the manufacture of acetone. At comparatively high temperatures butyl alcohol is decomposed partially to butadiene [31] but, as in many pyrolytic processes, the yields are small. The alcohol may be converted to the corresponding chloride and the resulting butyl chloride then chlorinated to the dichlorides which may then be decomposed by methods already mentioned, to butadiene,[32]

$$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CH_2Cl \longrightarrow \text{dichloride} \longrightarrow \text{butadiene}$$

By similar methods isoamyl alcohol, the chief constituent of fusel oil, may be converted by hydrogen chloride to isoamyl chloride, which on chlorination yields a mixture of dichlorides,

$(CH_3)_2CH.CHCl.CH_2Cl$	boiling-point	142° C.
$(CH_3)_2CCl.CH_2CH_2Cl$	" "	152° C.
$\begin{matrix} CH_2Cl \\ CH_3 \end{matrix}\!>\!CH.CH_2.CH_2Cl$	" "	170° C.

Of these dichlorides the second is the principal product, but the crude mixture, boiling-point 140°–180°, is used for the production of isoprene, the yield, according to Perkin,[33] being 40 per cent of the theory. As pointed out by Perkin the total available quantity of ordinary fusel oil, about 3500 tons, is wholly inadequate as a raw material for rub-

[29] Schmidt, Hochschwender & Eichler, U. S. Pat. 1,221,382.

[30] Fernbach & Strange, Brit. Pat. 15,203; 15,209; 16,925 (1910). The butyl alcohol contained in ordinary fusel oil from the manufacture of alcohol is isobutyl alcohol and is only a minor constituent.

[31] Perkin & Mathews, *J. Soc. Chem. Ind.* *32*, 884 (1913).

[32] Cf. Badische, German Pat. 255,519 (1913); 264,008 (1911); Harries, German Pat. 243,075; 243,076 (1910); Brit. Pat. 18,653; 22,035 (1912).

[33] *J. Soc. Chem. Ind.* *31*, 616 (1912).

ber synthesis, and is relatively high priced on account of its many industrial applications. The per cent of isoamyl alcohol in commercial fusel oil varies somewhat according to the distillation range over which it is collected, but the fraction distilling at 128°–131° contains approximately 87 per cent isoamyl and 13 per cent active amyl alcohol $C_2H_5CH(CH_3).CH_2OH$. Two typical analyses of commercial fusel oils are as follows,[34]

From fermentation of potatoes	*Per cent by wt.*	*From fermentation of corn*	*Per cent by wt.*
n.Butyl alcohol	6.8	n-Propyl alcohol	3.7
Isobutyl alcohol	24.3	Isobutyl alcohol	15.7
Amyl alcohols	67.8	Amyl alcohols	75.8
Fatty acids	.04	Hexyl alcohols	0.2(?)
		Fatty acids	.56

It is probable, in view of the researches of Ehrlich,[35] that such variations in the character of fusel oils are due to differences in the yeasts employed for fermentation or proteins otherwise introduced rather than the materials fermented. A sample of fusel oil from corn, examined by Pringsheim,[36] contained isopropyl and normal butyl alcohols in addition to the normal propyl and isobutyl alcohols which are normally present in fusel oil from this source.

In view of the efforts which have been made to utilize cheap fermentable material and the resulting butyl and amyl alcohols, as raw material for rubber synthesis, this phase of the work is reviewed here. Ehrlich claims that in ordinary yeast fermentation the fusel oil alcohols are derived from the decomposition of protein material, or rather the amino acids leucine, isoleucine and the like,

$$\underset{\text{leucine}}{(CH_3)_2CH.CH_2CH}\!<\!\begin{matrix}NH_2\\ CO_2H\end{matrix} + H_2O$$

$$\longrightarrow \underset{\text{isoamyl alcohol.}}{(CH_3)_2CH.CH_2CH_2OH} + CO_2 + NH_3$$

Ehrlich established the following relations,

(1) Pure yeast and pure sugar yields no fusel oil.
(2) " " " " " + leucine yields isoamyl alcohol.
(3) " " " " " + isoleucine yields d.amyl alcohol.

The addition of ammonium carbonate or asparagin to yeast fermentations decreases the yield of fusel oil and the addition of leucine, or

[34] "The Nitrocellulose Industry", Worden.
[35] Cf. Brit. Pat. 6,640 (1906); *Ber.* 40, 1027 (1907).
[36] *Biochem. Z.* 16, 243 (1909).

protein rich in this complex, increases it. Only traces of fusel oil are formed by alcoholic fermentation by means of Buchner's cell-free pressed yeast juice.[37] However, normal butyl alcohol at least can become, under certain conditions, one of the principal products derived from the sugar undergoing fermentation. Realizing the inadequacy of the supply of commercial fusel oil for possible rubber synthesis, Perkin and his associates undertook to develop a special process of fermentation which would yield larger proportions of butyl or amyl alcohols. Although the anaerobic *Bacillus butylicus* was discovered by Fitz [38] in 1878 in a study of glycerine fermentation, and Perdrix [39] had described an anaerobic bacterial fermentation which gave very high yields of fusel oil, it does not seem to have occurred to anyone else to utilize this possibility until it had been developed by Fernbach and Strange.[40] As has been previously noted both the major products of this fermentation, acetone and n.butyl alcohol, are necessary raw materials required by several different processes for the production of butadiene and dimethyl butadiene.

All of the known methods of decomposing alcohols to unsaturated hydrocarbons have been applied to the problem of producing these simple conjugated dienes. Butyleneglycol yields butadiene when passed over heated kaolin, alumina, or aluminum phosphate.[41] The butyleneglycol, required by this process, can be made from acetaldehyde, the primary raw material therefore being ethyl alcohol or acetylene. Acetaldehyde may be condensed by well-known methods to aldol, which upon reduction yields butylene glycol,

$$\text{Alcohol, or acetylene} \longrightarrow \text{acetaldehyde} \longrightarrow CH_3CH(OH).CH_2CHO$$

$$\longrightarrow CH_3CH(OH).CH_2CH_2OH \longrightarrow CH_2=CH.CH=CH_2$$

Butyraldehyde yields a certain amount of butadiene when passed over kaolin at 500°–600° under reduced pressure [42] and isovaleric aldehyde yields some isoprene under the same conditions.[43] Secondary butyl alcohol can be prepared by (1), reduction of the commercial solvent methyl ethyl ketone, derived from "acetone oil," or (2), treating oil gas with 80 per cent sulfuric acid and hydrolysing the butyl hydrogen

[37] Buchner & Meisenheimer, *Ber. 39,* 3201 (1906).
[38] *Ber. 11,* 481, 878 (1878).
[39] *Z. Spiritusind. 14,* 177 (1891).
[40] French Pat. 488,364 (1913).
[41] Mathews, Strange & Bliss, Brit. Pat. 3,873 (1912); Cf. Bayer, German Pat. 261,642 (1913).
[42] U. S. Pat. 1,033,327.
[43] U. S. Pat. 1,033,180.

sulfate so formed. The secondary butyl alcohol may then be decomposed catalytically, with very good yields, to butylene, which on chlorination or bromination and subsequent decomposition, yields butadiene. As has already been noted, it is very difficult completely to remove halogens from such substances on account of the stabilizing influence of an adjacent double bond, the second

$$(1)\quad CH_3CHBr.CHBr.CH_3 \longrightarrow CH_3CHBrCH = CH_2$$

$$(2)\quad CH_3CHBr.CH = CH_2 \longrightarrow CH_2 = CH - CH = CH_2$$

reaction taking place with difficulty (higher temperatures) and when the temperatures are sufficiently high for the complete removal of halogen, loss of the desired diene occurs through secondary reactions.

The condensation of acetaldehyde and ethyl alcohol by passing over heated copper, followed by decomposition of the condensation product by passing over heated alumina, has been noted by Ostromuislenski [44] as a possible method, and the chemical changes, which really involve five consecutive reactions, may be summarized as follows:

$$2C_2H_5OH \rightarrow CH_3CHO + C_2H_5OH \rightarrow CH_2 = CH.CH = CH_2 + 2H_2O$$

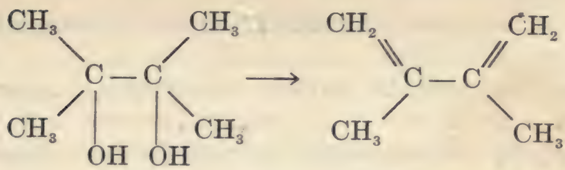
The yields of butadiene are poor and considering the number of other reactions which also occur in this process, it is not likely to become of industrial interest.

That tertiary alcohols are much more easily decomposed to unsaturated hydrocarbons, than secondary and primary alcohols, is well known, and advantage is taken of this fact in the employment of pinacone as an intermediate product. Thus acetone may be reduced and condensed to pinacone under a wide range of conditions and the use of amalgams for this purpose is particularly promising.[45] Pinacone is smoothly decomposed by passing over alumina at about 400° giving good yields of dimethylbutadiene.[46]

acetylene }
acetate of lime } ⟶ acetic acid ↘

starches and sugars } ⟶ acetone ⟶
starches and sugars ⟶

[44] *J. Russ. Phys.-Chem. Soc.* *47*, 1472, 1494 (1915) ; *J. Chem. Soc. Abs.* *1916*, I, 4.
[45] Holleman, *Rec. trav. chim.* *25*, 206 (1906) ; *Bull. soc. chim.* *1910*, 454.
[46] German Pat. 250,086.



dimethylbutadiene

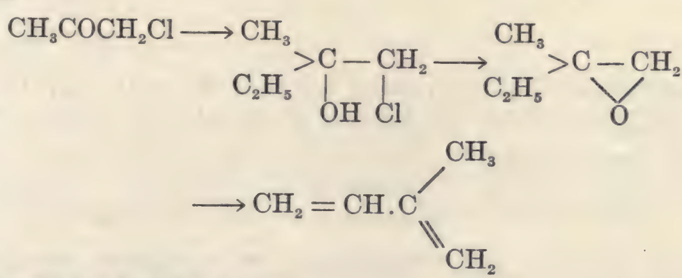
The synthetic rubber manufactured in Germany during the recent war was made from pinacone and dimethylbutadiene, the latter material being polymerized in sealed iron drums during a period of several months.

Pinacone chlorohydrin also yields dimethylbutadiene, when heated with bases, dimethylaniline being recommended for this purpose,[47] and Kondakow[48] claims that pinacone dichloride gives better yields of the diene than pinacone itself. Decomposition of the alcohol pentene-2, ol-4 by passing over alumina or kaolin at 400° has been employed for the preparation of piperylene. Under certain conditions acetaldehyde condenses to crotonic aldehyde and on methylating this aldehyde pentene-2, ol-4 is formed.

$$2CH_3CHO \longrightarrow CH_3CH=CH.CHO \longrightarrow CH_3CH=CH.CH<\begin{matrix}OH\\CH_3\end{matrix}$$

$$\longrightarrow CH_3CH=CH.CH=CH_2$$

Many methods have been described which make use of well-known syntheses, but which are interesting from a theoretical point of view. Kyriakides[49] has described an interesting synthesis starting with chloroacetone, which is ethylated, and the resulting chlorohydrine is then treated with caustic alkali to obtain the oxide, as indicated in the following,



[47] German Pat. 319,505 (1916).
[48] *J. prakt. Chem.* 62, 169 (1900).
[49] *J. Am. Chem. Soc.* 36, 663 (1914).

The oxide is decomposed by heating in the presence of kaolin at 440°–460°.

Dimethylallene may be partially converted into isoprene by rearrangement [50] and Ipatiev [51] has prepared isoprene from this hydrocarbon by adding two molecules of hydrogen bromide, followed by decomposing the dibromide by well-known methods,

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>C=C=CH_2 + 2HBr \longrightarrow \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>CBr.CH_2CH_2Br$$

$$\longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_3 \end{matrix}\!\!\!\!\! \diagdown\!\!\!\! \diagup C-CH=CH_2$$

Among the reactions of theoretical interest which have been employed in research in this field, may be mentioned Euler's [52] preparation of isoprene by the exhaustive methylation of methylpyrollidine, as follows,

$$\begin{matrix} CH_3-CH & -CH_2 \\ | & \\ CH_2 & -CH_2 \end{matrix}\!\!>NH + 2CH_3I + NaOH \longrightarrow$$

$$\begin{matrix} CH_3-CH & -CH_2 \\ | & \\ CH^2 & -CH_2 \end{matrix}\!\!>N(CH_3)_2I \longrightarrow \begin{matrix} CH_3-C & = & CH_2 \\ | & & \\ CH_2- & CH_2- & N(CH_3)_2 \end{matrix}$$

$$\xrightarrow{+\,CH_3I} \begin{matrix} CH_3-C & = & CH_2 \\ | & & \\ CH_2- & CH_2- & N(CH_3)_3I \end{matrix} \xrightarrow{+\,KOH} \begin{matrix} CH_3-C & = & CH_2 \\ | & & \\ CH & = & CH_2 \end{matrix}$$

isoprene

It will be recalled that this method has been frequently used by von Braun and others in the investigation of alkaloids, on account of the ease with which nitrogen can be removed from organic bases.

Phenol may readily be hydrogenated to cyclohexanol, which on oxidation by nitric acid [53] yields adipic acid. Conversion of this acid to

[50] Webel (U. S. Pat. 1,083,164), claims that *as.* dimethylallene rearranges to isoprene when passed over alumina at 300°, and preferably under diminished pressure.
[51] *J. prakt. Chem.* *55,* 4 (1897).
[52] *J. prakt. Chem.* *57,* 132 (1898).
[53] Bouveault and Locquin, *Bull. Soc. chim.* *1908, 3,* 437.

the amide, followed by treatment with hypochlorite, yields tetramethylenediamine and the method of exhaustive methylation applied to this diamine yields butadiene; cresol, treated similarly, yields isoprene.

Polymerization of Conjugated Dienes to Rubber-like Substances.

As pointed out elsewhere in these pages the polymerization of isoprene had been observed by Greville Williams, Bouchardat, Tilden and Wallach. But the first attempt to polymerize isoprene which had been prepared from sources other than rubber itself was Tilden's investigation of isoprene made by the pyrolysis of turpentine, published in 1888.[54] Tilden states that, "The action of hydrochloric acid on isoprene converts it partially into caoutchouc; the latter seems to be obtained more easily starting with the oily polymeride resulting from the action of heat." Some 28 years later, Ostromuislenski [55] showed clearly that the character of synthetic isoprene rubber was markedly affected by the method of polymerization; that on heating isoprene to 80°–90° it undergoes spontaneous polymerization to a dimeride, β-myrcene, and this hydrocarbon then yields "normal" caoutchouc when polymerized by sodium, or barium peroxide. However, when isoprene itself is treated with these reagents the resulting rubber is not normal.[56] Tilden seems to have been aware all along that rubber might be formed by the polymerization of isoprene. The polymerization of the isomeric hydrocarbon piperylene, $CH_3CH = CH — CH = CH_2$ had been observed by Hofman [57] and by Schotten,[58] but their publications contain no suggestion that their product resembled rubber. In 1892 Tilden,[59] in a communication to the Philosophical Society of Birmingham, stated, "I was very much surprised to find that the contents of the flasks containing isoprene, prepared from turpentine, had entirely altered in appearance. Instead of a colorless, limpid liquid, there was now a thick syrup, in which floated several pieces of a yellow solid material. On examining it more closely this was found to be caoutchouc." * * * "A solution of synthetic rubber leaves, on evaporation, a residue which completely resembles in all its characteristics a like preparation made with Para rubber." * * * "Artificial rubber combines with sulfur in the same way as natural rubber, giving an elastic, resistant mass." A little later Tilden's results were con-

[54] *J. Chem. Soc.* *45*, 411 (1888).
[55] *J. Russ. Phys.-Chem. Soc.* *48*, 1071 (1916).
[56] *J. Russ. Phys.-Chem. Soc.* *47*, 1928 (1915).
[57] *Ber.* *14*, 665 (1881).
[58] *Ber.* *15*, 425 (1882).
[59] *Chem. News.* *65*, 265 (1895).

firmed by Weber[60] who prepared about 200 grams of synthetic isoprene rubber, and Pickles[61] also confirmed Tilden's statement that isoprene polymerizes on standing in contact with air.

The marked influence of oxygen upon the formation of polymers is well shown by experiments reported by Engler,[62] in which duplicate samples were exposed to oxygen and carbon dioxide, at 80° C. The very rapid polymerization of styrene, and the conjugated dienes, isoprene and myrcene, are particularly noteworthy.

PER CENT POLYMERS FORMED ON STANDING.

	In contact with CO_2				*In contact with O_2*			
Days exposed	*1*	*2*	*3*	*4*	*1*	*2*	*3*	*4*
Limonene	2%	4%	5%	8%	4%	6%	8%	9%
Phellandrene	4	6	8	9	9	13	16	21
Pinene	1	2	2	3	3	4	4	5
Myrcene	8	13	18	22	20	30	40	50
Camphene	3	4	5	6	5	7	8	9
Isoprene	14 per cent in 10 hours;				35 per cent, 10 hours			
Styrene	22 per cent, 20 hours;				67 per cent, 20 hours			

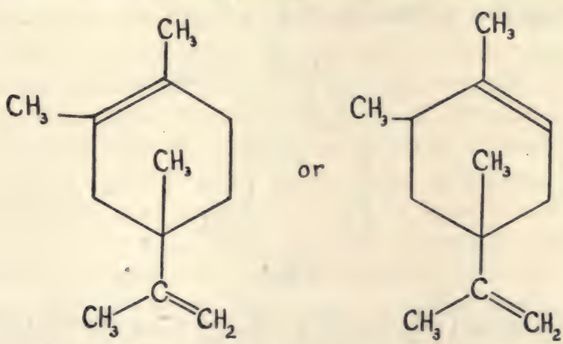
The presence of moisture apparently has no effect upon the rate of polymerization of hydrocarbons, although the smallest trace of moisture acts catalytically upon the polymerization of the aldehyde, glyoxal;[63] monomolecular succinic dialdehyde behaves in a similar manner.

The polymerization of dimethyl butadiene, dimethyl 2-3 butadiene 1-3, to a rubber-like substance was first effected by Kondakow,[64] who noted that it polymerized spontaneously and more rapidly than isoprene or butadiene. His publications upon the polymerization of this dimethylbutadiene, which he prepared from pinacone, would seem to justify Kondakow's claims of priority, so far as the dimethylbutadiene process, later patented and used industrially in Germany, is concerned. It was noted also, and confirmed by others,[65] that when dimethyl butadiene polymerizes, either spontaneously or in the presence of alcoholic caustic potash, a dimeride and a trimeride are produced, in addition to the rubber-like substance. It was important for the technicalities of later patent controversies that Kondakow had described his dimethylbutadiene rubber as insoluble in most organic solvents, although it is now generally recognized that this property varies considerably

[60] *J. Soc. Chem. Ind. 13,* 11 (1894).
[61] *J. Chem. Soc. 97,* 1085 (1910).
[62] *8th Int. Congr. Appl. Chem. 25,* 661 (1912).
[63] Harries, *Ber. 40,* 165 (1906) ; *41,* 255 (1908).
[64] *J. prakt. Chem. 64,* 109 (1901).
[65] Lebedew, *J. Russ. Phys.-Chem. Soc. 41,* 1818 (1909) ; Harries, *Ann. 383,* 210 (1911).

with all rubbers, depending upon the degree of polymerization; in fact, vulcanization is essentially a process of effecting higher degrees of polymerization. It is well known also that dimethylbutadiene polymerizes more rapidly than other similar hydrocarbons. Perkin states, "The situation in 1906 might be summed up in this way; it had been recognized, in a more or less general way, that most compounds containing a system of conjugated double linkings, show a tendency to polymerize, more or less readily. The polymerides are either viscous, ill defined substances, or well characterized caoutchoucs; or, again, hard resinous solids, like polystyrene. Their properties vary according to their method of preparation, and according to the molecular weight of the hydrocarbon employed as a raw material."

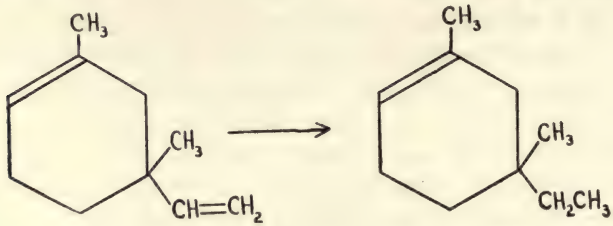
Like natural Para rubber, Kondakow's rubber can be *depolymerized* by heat, although more readily than Para rubber, the principal product being a dimeric dimethylbutadiene resembling dipentene and which Richard [66] and Kondakow regard as having the structure,



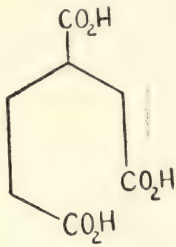
The same hydrocarbon is also formed by careful polymerization of 2.3-dimethylbutadiene-(1.3). In the polymerization of isoprene to synthetic isoprene rubber a dimeric isoprene is formed, in addition to the dimeride, dipentene. This second hydrocarbon, called di-isoprene or myrcene by earlier writers, yields a *liquid* tetrabromide, in contrast to the crystalline dipentene tetrabromide. According to Lebedew

[66] *Compt. rend.* *153*, 116 (1911); According to Lebedew and Mereshkowski (*J. Russ. Phys.-Chem. Soc.* *45*, 1249 [1913]) this dimeride has the following properties; boiling-point 85° at 13 mm., 205° at 750 mm., $D^{0°}_{4°}$ 0.8741 n_D 1.48074; dry HCl yields a monohydrochloride $\mathrm{MeC}\begin{matrix}/\!/\mathrm{C.Me.CH_2} \\ \diagdown \mathrm{CH_2CH_2}\end{matrix}\!\!>\mathrm{C.Me.CCl}\begin{matrix}\diagup \mathrm{Me} \\ \diagdown \mathrm{Me}\end{matrix}$, boiling at 122°-124° under 17 mm.; oxidation by benzoyl peroxide, according to Prileschajev (q.v.) yields a dioxide which is hydrolyzed by aqueous benzoic acid to a tetrahydric alcohol.

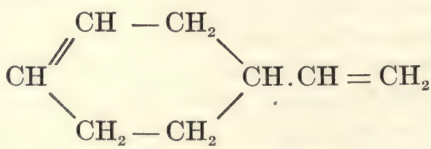
and Mereshkowski [67] this hydrocarbon is 1.3-dimethyl-3-ethenyl-Δ^6-cyclohexene.[68] On hydrogenating in the presence of platinum the side chain ethenyl group is first saturated, following the general behavior of substances containing double bonds in both the ring and side chain.



Piperylene similarly should yield two dimerides. Butadiene yields a dimeride, C_8H_{12}, boiling at 36° under 23 mm., 129.5°–131° under 760 mm. pressure. Hydrogenation by Paal's method yields ethyl cyclohexane; bromine reacts to form a tetrabromide melting at 69.5°–70.5° and oxidation yields the acid



from which facts, and reasoning by analogy from the relations between isoprene and dipentene, Lebedew [69] concludes that the hydrocarbon is 1-ethenyl-Δ^4-cyclohexene,



These details are of first importance as the yield of synthetic rubber, by present methods of polymerization, is seriously diminished by the formation of these oily polymers.

As to why or how sodium effects the polymerization of isoprene,

[67] *Loc. cit.*
[68] Cf. Harries, *Ann. 383*, 157 (1911).
[69] *J. Russ. Phys.-Chem. Soc. 43*, 1124 (1911).

no one has hazarded a theory. Perkin[70] relates that Weizmann and Mathews were induced to try the effect of permitting the hydrocarbon to stand in contact with the metal, by their having noted the conversion of dimethylallene to isopropylacetylene by metallic sodium,

$$(CH_3)_2C = C = CH_2 \qquad\qquad (CH_3)_2CH - C \equiv CH,$$

a reaction which had been recorded by Favorsky.[71] This discovery, the polymerization of isoprene by sodium, was, according to Perkin, made by Weizmann and Mathews in July and August, 1910, although it was first publicly described in the following year by Harries.[72] The same discovery had evidently been made by Harries in the "end of (the year) 1910."

The polymerization of hydrocarbons may, according to Lebedew and Mereshkowski[73] be grouped in several well defined classes, (1), the *styrene* type, peculiar to ethylene hydrocarbons with unsymmetrical substitution of the hydrogen atoms by phenyl, or other groups, and yielding amorphous polymers of very high molecular weight and whose structures are not yet known; (2) the *stilbene* type, shown by substances having symmetrically substituted groups; (3) the *acetylene* type, whose characteristic is the formation of benzene or its derivatives; (4) the *allene* type, yielding cyclobutane derivatives; (5) the 1.3-*butadiene or isoprene* type, which forms cyclohexane derivatives and also polymers of high molecular weight, usually amorphous, and including rubber-like substances. The structures of the polymers of the styrene and stilbene type, when ascertained, may show that these two classes are really of the same type of polymerization.

With isoprene and 2.3-dimethylbutadiene-(1.3) it has been shown that with increasing temperature the proportion of the dimeride increases and that of the rubber-like polymer decreases. Since the reaction is markedly affected by catalysts, it follows that, for maximum yields of "synthetic rubber," a catalyst and the lowest possible temperature should be employed. The search for raw materials for the preparation of the simpler conjugated dienes, and the effort to discover efficient methods for the preparation of these hydrocarbons has involved a great deal of research. The finishing step in the process, polymerization, is still without a theory sufficiently tangible or plausible to be of use as a guide for further work. There has been a very noticeable

[70] *Loc. cit.*
[71] *J. Russ. Phys.-Chem. Soc. 19,* 558 (1887).
[72] *Ann. 383,* 157 (1911).
[73] *J. Russ. Phys.-Chem. Soc. 45,* 1249 (1913); *J. Chem. Soc. Abs. 1913,* I, 1285.

abatement of research on rubber synthesis since 1912 (the manufacture of synthetic rubber may have been, for Germany, a war preparedness measure). It is certain that all methods of synthesis previously known have been applied to this problem,—and synthetic rubber has not yet made a place for itself. New methods of synthesis or polymerization, or changed economic values with respect to raw materials for synthesis, or cost of plantation rubber, may affect the situation in ways which none can now foresee.

PROPERTIES OF THE SIMPLER CONJUGATED DIENES.

Substance	*Structure*	*Boiling-Point °C*	*Specific Gravity*	*Refractive Index* $N\frac{20°}{D}$	*Characteristic Derivative*
Butadiene	$CH_2=CH-CH=CH_2$	$-5°$ to $-4°$ (1) (2)	....	......	tetrabromide { M.-P. 118° { M.-P. 39°–40°
		33.5° (3)	$0.6989\frac{0°}{0°}$ (3)	1.4041	dichlorohydrine
Isoprene	$CH_2=C(CH_3)-CH=CH_2$			(4)	M.-P. 81° (3)
		33.75° to 34.00° (5)	$0.6794\frac{19°}{0°}$		
			$0.6867\frac{16.5°}{4°}$ (5)	1.42617	nitrosochloride
		34.5°–35° (7)		(5)	M.-P. 81°–82° (6)
Piperylene	$CH(CH_3)=CH-CH=CH_2$	42. ° (8)	$0.6952\frac{0°}{0°}$ (9)		tetrabromide
				1.4206	M.-P. 114°
			$0.6794\frac{25°}{4°}$ (10)	(10)	
Dimethyl-butadiene;	$CH_2=C(CH_3)-C(CH_3)=CH_2$		$0.7446\frac{0°}{0°}$ 11)		nitrosate
					M.-P. 72°–73°
		69.5 (11)			
2, 3-dimethyl-butadiene (1, 3)			$0.7273\frac{20°}{20°}$ **(11)**	1.4377	(12)
				(11)	

Observer:

1 Thiele, *Ann. 308*, 337.
2 Grimaux and Cloez, *Bull. soc. chim.* (2), *48*, 31.
3 Mokijewski, *Chem. Zentr. 1899*, I, 589.
4 Gladstone, *J. Chem. Soc. 49*, 623 (1886).
5 Harries, *Ber. 47*, 1999 (1914).
6 Tilden, *J. Chem. Soc. 45*, 414 (1884).
7 Lebedew, *J. Chem. Soc. Abs. 1913*, I, 1288.
8 Hofman, *Ber. 14*, 664 (1881).
9 Wosnesenski, *Chem. Zentr. 1904*, II, 183.
10 Reif, *Ber. 41*, 2744 (1908).
11 Kondakow, *J. prakt. Chem.* (2) *62*, 172 (1900).
12 Couturier, *Ann. chim. phys.* (6) *26*, 493 (1892).

Name	Boiling-Point	Density	n_D	Remarks	References
$\Delta^{2,4}$-Hexadiene	80. °– 82. °	0.72656 $\left(\frac{0°}{4°}\right)$			
		0.7177 $\left(\frac{21°}{4°}\right)$	1.4463 (21. °)	tetrabromide M.-P. 80°	1
3-Methyl-$\Delta^{2,4}$-pentadiene	76. °– 79. °	0.7576 $\left(\frac{0°}{4°}\right)$	1.45427 (16.5°)	tetrabromide, oil	2
$\Delta^{1,3,5}$-Hexatriene	80. °– 80.5° (M.-P. -11°)	0.740 $\left(\frac{14°}{4°}\right)$	1.517 (14. °)	crystalline dibromide	3
$\Delta^{2,4}$-Heptadiene	104. °–106. °	0.75099 $\left(\frac{0°}{4°}\right)$	1.4486 (21.5°)	tetrabromide in 2 forms,	
		0.7327 $\left(\frac{21.5°}{4°}\right)$		oil and crystals, M.-P. 112°	1
3-Methyl-$\Delta^{2,4}$-hexadiene	107. °–108. °	0.7753 $\left(\frac{0°}{4°}\right)$	1.46146 (15. °)	from 3-methyl-Δ^{2}-hexene-ol(4)	2
4-Methyl-$\Delta^{3,5}$-hexadiene	101. °–103. °	0.7404 $\left(\frac{25°}{4°}\right)$	1.45247 (25. °)	....	4
$\Delta^{1,3,5}$-Heptatriene	112. °	.....	......	by cond. $CH_3CH=CH.CHO$ by Zn in ether	5
3-Methyl-$\Delta^{2,4}$-heptadiene	132. °–135. °	0.7783 $\left(\frac{0°}{4°}\right)$	1.4693 (14.7°)	....	2
6-Methyl-$\Delta^{2,4}$-heptadiene	114. °–116. °	0.7516 $\left(\frac{0°}{4°}\right)$	1.4397 (25. °)	....	1
3.5-Dimethyl-$\Delta^{2,4}$-hexadiene	114. °–115. °	0.7714 $\left(\frac{0°}{4°}\right)$	1.4545 (16.5°)	....	4
4-Methyl-$\Delta^{3,5}$-octadiene	148. °–151. °	0.7640 $\left(\frac{25°}{4°}\right)$	1.4628 (25. °)	....	4
7-Methyl-$\Delta^{2,4}$-octadiene	149. °	0.7653 $\left(\frac{0°}{4°}\right)$	1.45 ?	tetrabromide, oil	1
3.5-Dimethyl-$\Delta^{2,4}$-heptadiene	144. °–146. °	0.7853 $\left(\frac{0°}{0°}\right)$	1.4633 (14. °)	....	2
2.7-Dimethyl-$\Delta^{2,7}$-octadiene	163.5°–164.5°	.....	......	by CH_3MgI on ethyl adipate	6
3.7-Dimethyl-$\Delta^{2,4}$-octadiene	164. °–167. °	0.7939 $\left(\frac{0°}{4°}\right)$	1.4665 (14.5°)	....	2

1 Reif, *Ber.* *41*, 2739 (1908).
2 Abelmann, *Ber.* *43*, 1574 (1910).
3 van Romburg and Muller, *Chem. Abs.* *8*, 3036 (1914).
4 Bjelouss, *Ber.* *45*, 625 (1912).
5 Enklaar, *Chem. Weekblad.* *10*, 60 (1913); *Chem. Abs.* *7*, 1169 (1913).
6 Bouveault, *Bull. soc. chim.* *17*, 202 (1915).

Chapter VII. Cyclic Non-benzenoid Hydrocarbons.

General Methods of Synthesis of Cyclic Non-benzenoid Hydrocarbons.

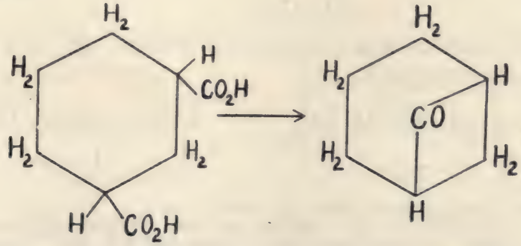
Many of the well-known condensation reactions of the paraffine series can take place with intramolecular condensation or ring formation. Thus the type condensation of acetic ester to acetoacetic ester can take place with the diethyl esters of adipic, pimelic and suberic acids to form 5, 6 and 7 carbon rings, respectively, for example,

$$CH_2{<}\begin{matrix} CH_2CH_2.CO_2C_2H_5 \\ CH_2CH_2.CO_2C_2H_5 \end{matrix} \qquad CH_2{<}\begin{matrix} CH_2 - CH_2 \\ \\ CH_2 - CH.CO_2C_2H_5 \end{matrix}{>}CO$$

Glutaric and succinic esters do not condense in this manner to give cyclobutane and cyclopropane derivatives, illustrating the relative difficulty with which ring structures of 3 or 4 carbon atoms are formed. The calcium salts of adipic, pimelic and suberic acids give, on heating, cyclopentanone, cyclohexanone and cycloheptanone respectively, but calcium succinate gives the cyclic diketone

$$\begin{matrix} CH_2 - CO - CH_2 \\ | \qquad\qquad\quad | \\ CH_2 - CO - CH_2 \end{matrix}$$

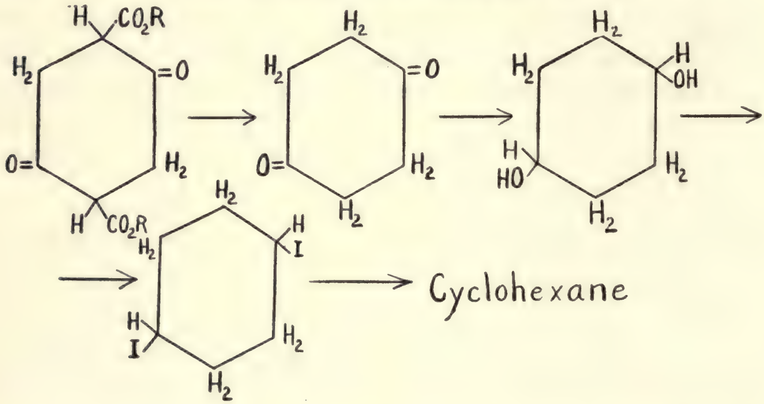
When the calcium salt of cyclohexane -1.3-dicarboxylic acid is decomposed by heat the bicyclic ketone is formed which Stark[1] calls "demethylated pinone."



[1] *Ber.* 45, 2369 (1912); this ketone boils at 157°-158°, d_{20} 0.9322; semicarbazone melting-point 179°-180°.

Ring closing incidental to Grignard's synthesis of carboxylic acids has been observed, as in the case of 1.5-dibromopentane, which with magnesium forms the dimagnesium compound, and then on treating with carbon dioxide yields *cyclohexanone* and pimelic acid.[2]

Succinic ester and sodium condense to give a six carbon ring, succinosuccinic ester. On hydrolyzing and heating with sulfuric acid the cyclic diketone is obtained which may be reduced to cyclohexane by converting it first into the alcohol, cyclohexanediol-1.4, then into the corresponding iodide and reducing this with zinc dust and acetic acid, exactly as in the case of aliphatic alcohols and iodides.



The method of Würtz and Fittig, of treating alkyl halides with metallic sodium effecting condensation with formation of sodium halide, has been employed for ring formation. Freund made cyclopropane by treating trimethylene bromide with sodium.[3]

$$CH_2 < \begin{matrix} CH_2Br \\ CH_2Br \end{matrix} + Na_2 \longrightarrow CH_2 < \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + 2NaBr.$$

Methyl cyclobutane was prepared by Perkin, Jr., in a similar way from 1.4 dibromopentane.[4]

$$\begin{matrix} CH_2 - CHBr.CH_3 \\ | \\ CH_2 - CH_2Br \end{matrix} + Na_2 \longrightarrow \begin{matrix} CH_2 - CH - CH_3 \\ | \quad\quad\; | \quad\quad \\ CH_2 - CH_2 \quad\; \end{matrix}$$

[2] Grignard & Vignon, *Compt. rend.* *144*, 1358 (1907).
[3] *Monatsh 3*, 625 (1882). The original material for this synthesis, trimethylene glycol is now a common commercial product, being isolated from the forerunnings in glycerine distillation.
[4] *J. Chem. Soc. 53*, 201 (1888); *65*, 599 (1894).

and cyclohexane has been made from 1.6-dibromohexane and sodium.

Condensations to carbocyclic derivatives have also been made as indicated by the following synthesis; the disodium compound of acetone dicarboxylic ester being treated with iodine [5] gives,

$$CO<\begin{array}{l} CO_2R \qquad\qquad\quad CO_2R \\ |\qquad\qquad\qquad\quad\;\; | \\ CHNa + I_2 + NaHC \\ CHNa + I_2 + NaHC \\ |\qquad\qquad\qquad\quad\;\; | \\ CO_2R \qquad\qquad\quad CO_2R \end{array}>CO \longrightarrow CO<\begin{array}{l} CO_2R\;\; CO_2R \\ |\qquad\quad | \\ CH - CH \\ CH - CH \\ |\qquad\quad | \\ CO_2R\;\; CO_2R \end{array}>CO$$

Instead of using free iodine or bromine, alkyl halides may react with sodium malonic ester or similar sodium compounds, as in the following syntheses carried out by W. H. Perkin, Jr.[6]

$$\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array} + CH_2<\begin{array}{l} CO_2R \\ CO_2R \end{array} + 2CH_3ONa \longrightarrow \begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}>C<\begin{array}{l} CO_2R \\ CO_2R \end{array}$$

from which cyclopropane monocarboxylic acid is readily made by loss of CO_2 from the dibasic acid.

In the same way trimethylene bromide (1) and pentamethylene bromide (2) yield

$$(1) \longrightarrow CH_2<\begin{array}{l} CH_2 \\ CH_2 \end{array}>CH.CO_2H \qquad \textit{cyclobutanecarboxylic acid}$$

$$(2) \longrightarrow CH_2<\begin{array}{l} CH_2 - CH_2 \\ CH_2 - CH_2 \end{array}>CH.CO_2H \qquad \textit{cyclohexanecarboxylic acid}$$

The above syntheses are capable of considerable variation and extension as the following syntheses indicate:

$$(1)\quad \begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} + \begin{array}{l} CH_2(CO_2R)_2 \\ \\ CH_2(CO_2R)_2 \end{array} + 2C_2H_5ONa \rightarrow \begin{array}{l} CH_2 - CH(CO_2R)_2 \\ | \\ CH_2 - CH(CO_2R)_2 \end{array}$$

$$\begin{array}{l} CH_2 - CNa(CO_2R)_2 \\ | \\ CH_2 - CNa(CO_2R)_2 \end{array} + Br_2 \rightarrow \begin{array}{l} CH_2 - CH(CO_2R)_2 \\ |\qquad\quad | \\ CH_2 - CH(CO_2R)_2 \end{array} \rightarrow$$

$$\begin{array}{l} CH_2 - CH.CO_2H \\ |\qquad\quad | \\ CH_2 - CH.CO_2H \end{array}$$

[5] v. Pechmann, *Ber.* *30*, 2569 (1897).
[6] *Ber.* *35*, 2091 (1902).

(2)

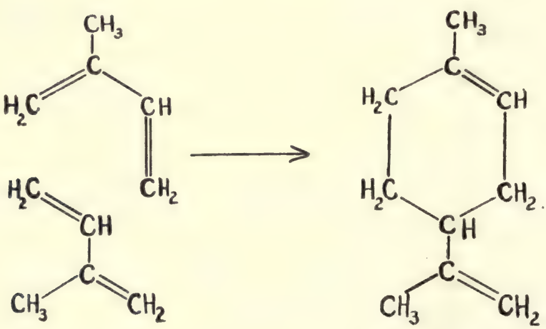
$$CH_2\!<\!\begin{array}{l}CH_2 - CNa(CO_2R)_2\\ CH_2 - CNa(CO_2R)_2\end{array} + CH_2I_2 \rightarrow CH_2\!\begin{array}{l}\diagup\; CH_2 - C(CO_2R)_2 \;\diagdown\\ \qquad\qquad\qquad\qquad\qquad\quad CH_2\\ \diagdown\; CH_2 - C(CO_2R)_2 \;\diagup\end{array}$$

$$\rightarrow CH_2\!<\!\begin{array}{l}CH_2 - CH.CO_2H\\ \qquad\qquad >CH_2\\ CH_2 - CH.CO_2H\end{array}$$

Acetoacetic ester and ethylene bromide yield cyclopropyl methyl ketone in the following manner:

$$\begin{array}{l}CH_2Br\\ |\\ CH_2Br\end{array} + \begin{array}{c}CH_3\\ |\\ CO\\ |\\ H_2C\\ |\\ CO_2R\end{array} + 2C_2H_5ONa \rightarrow \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!>\!\begin{array}{c}CH_3\\ |\\ CO\\ |\\ C\\ |\\ CO_2R\end{array} \rightarrow \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!>\!CH.CO.CH_3$$

Polymerization of unsaturated substances sometimes results in ring formation, as in the condensation of isoprene to dipentene and isoprene-rubber.

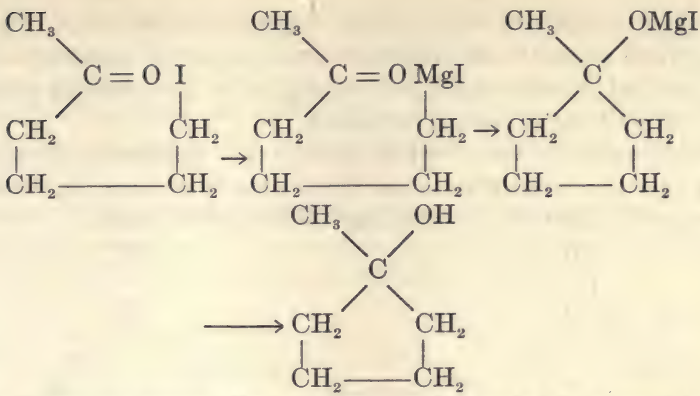


Vinylacrylic acid also polymerizes readily, in the following manner,[7] when heated with barium hydroxide.

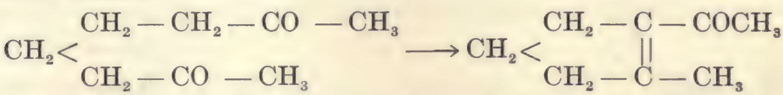
$$\begin{array}{l}CH_2 = CH.CH = CH.CO_2H.\\ \\ CH_2 = CH.CH = CH.CO_2H.\end{array} \longrightarrow \begin{array}{l}CH_2.CH = CH.CH_2\\ |\qquad\qquad\qquad\quad |\\ CH_2.CH = CH.CH_2\end{array}$$

The Grignard reaction has also been employed to effect ring closing as in the preparation of 1-methyl-1-hydroxycyclopentane by Zelinsky and Moser.[8]

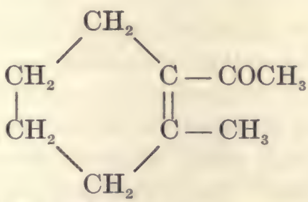
[7] Döbner, *Ber.* 35, 2129 (1902).
[8] *Ber.* 35, 2684 (1902).



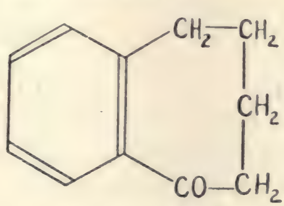
In the same manner that acetone condenses to give mesityl oxide, diacetylbutane treated with sulfuric acid yields methylcyclopentene-methyl ketone.[9]



Diacetylpentane when similarly treated yields a methylcyclohexenemethyl ketone.



Condensation of alkyl halides with benzenoid hydrocarbons, with elimination of halogen acid, takes place very rapidly in the presence of anhydrous aluminum chloride (the Friedel-Crafts synthesis). This reaction has been employed for ring closing, as, for example, phenylvaleryl chloride being converted into

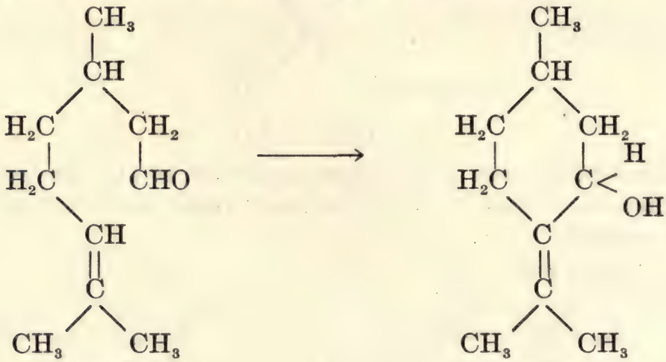


benzo-cycloheptanone

[9] Kipping & Perkin, *J. Chem. Soc.* 57, 14, 24 (1890).

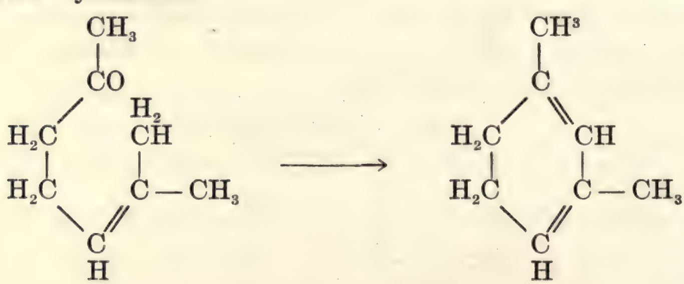
Halogen acids are very readily eliminated from alkyl chlorides alone, when treated with aluminum chloride, as for example, chloropentanes and chlorohexanes, but the nature of the resulting products has apparently never been investigated.

Condensation of the aldehyde citronellal to isopulegol, through the action of acetic anhydride, is not typical but illustrates the tendency, so frequently observed, to form rings of six carbon atoms.



citronellal *isopulegol*

Methylheptenone is condensed by dehydrating agents to a mixture of *m*-xylene and 1.3-dimethyl-Δ^3-cyclohexene. The initial reaction product apparently is 1.3-dimethyl-$\Delta^{1 \cdot 3}$-cyclohexadiene, which it will be noted has the same arrangement of the double bonds as in α-terpinene and the ease with which terpinene is converted to cymene is well known. Apparently this cyclohexadiene derivative undergoes auto-reduction to give about equal parts of *m*-xylene and 1.3-dimethyl-Δ^3-cyclohexene.[10]

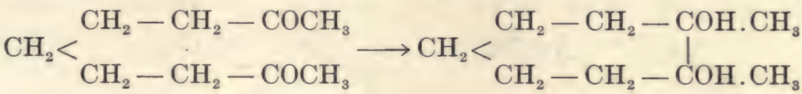


The condensation of pseudo-ionone to α and β-ionone by means of sulfuric acid is supposed to take place through the addition and subse-

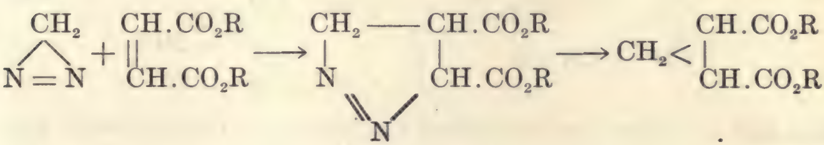
[10] Wallach, *Ann.* 395, 74 (1913).

quent loss of water. The discovery of this reaction (and the formation of pseudo-ionone from citral and acetone by the action of barium hydrate or other alkalies) by Tiemann and Kruger,[11] in 1882 marked the beginning of the industrial manufacture of this now well-known "synthetic violet" perfume. The two ionones are cyclohexane derivatives (see p. 201).

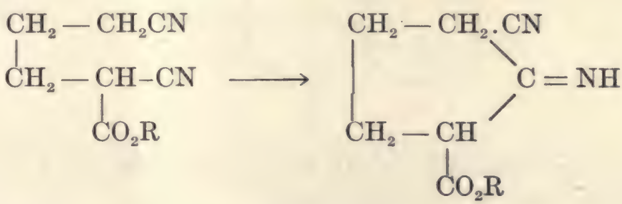
Pinacone condensation may take place intramolecularly to form carbocyclic structures, as for example, the formation of 1.2-dimethyl-1.2-dihydroxycycloheptane from diacetylpentane.[12]



A special synthesis, that of cyclopropane derivatives, has been effected by means of diazomethane or diazoacetic ester by Buchner and Curtius.[13] Thus fumaric ester and diazomethane yield cyclopropane-dicarboxylic ester.

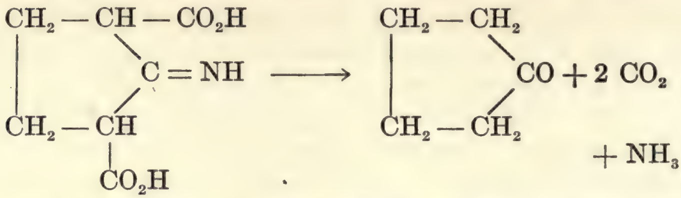


Cyclopentanone has been made by applying the method of condensing nitriles in the presence of sodium ethylate, a reaction discovered by Thorpe.[14] Thus 1.4-dicyano-valeric ester condenses to the imino compound.

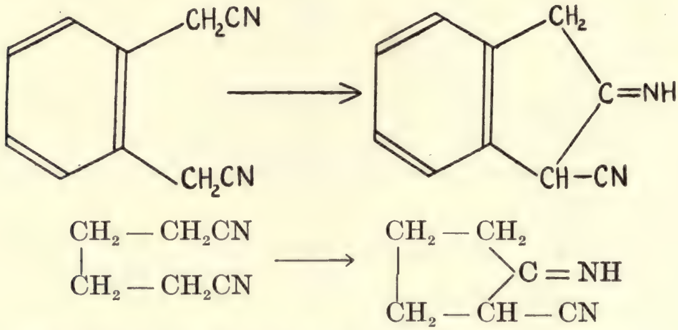


On hydrolyzing by means of sulfuric acid and heating the resulting acids the imino group is replaced by oxygen and two molecules of CO_2 are removed, resulting in cyclopentanone.

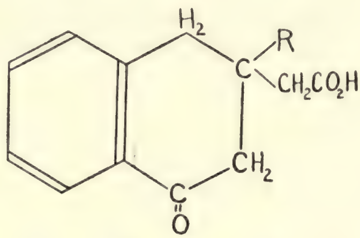
[11] *Ber. 31*, 808 (1898).
[12] Kipping & Perkin, *J. Chem. Soc. 59*, 214 (1891).
[13] *Ber. 18*, 237 (1885).
[14] *J. Chem. Soc. 85*, 1726 (1904); *91*, 578, 1004 (1907).



It has been shown by Thorpe[15] that ring closing to form rings of five carbon atoms takes place very rapidly and with approximately equal ease in both the following cases,



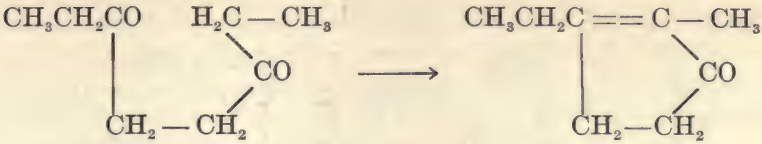
Kon and Stevenson also find[16] that ring closing by elimination of water from the COOH group takes place readily forming products of the following type.



There is no indication of the valency direction being different in any of these examples of ring closing.

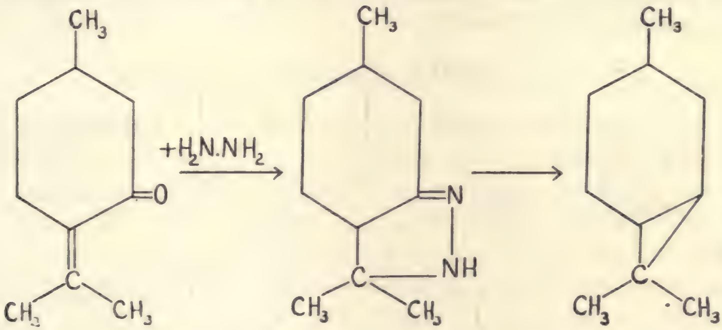
An instance of the ease with which substances containing a five-carbon ring are formed is the condensation of *sym.*-dipropionylethane to 1-methyl-5-ethyl-Δ^5-cyclopentene-2-one by the action of 10 per cent aqueous caustic potash.[17]

[15] *J. Chem. Soc.* **93**, 165 (1908); **95**, 1901 (1909).
[16] *J. Chem. Soc.* **119**, 87 (1921).
[17] Blaise, *Compt. rend.* **158**, 708 (1914).

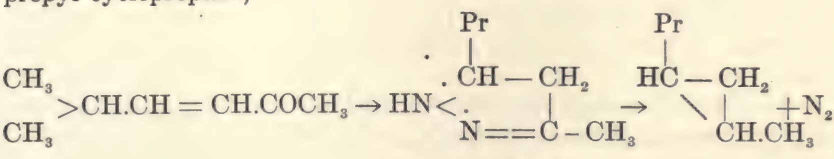


Acetonylacetone and acetonylacetophenone are unchanged under these conditions.

Kishner[18] has discovered that when hydrazine reacts upon unsaturated ketones containing the group $-CH=CH.CO$-pyrazoline bases are formed in many instances, which are readily decomposed to give cyclopropane derivatives. Thus pulegone yields carane:



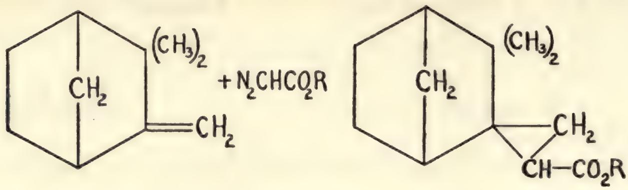
In a similar manner, isobutylidene acetone yields 1-methyl-2-isopropyl-cyclopropane,



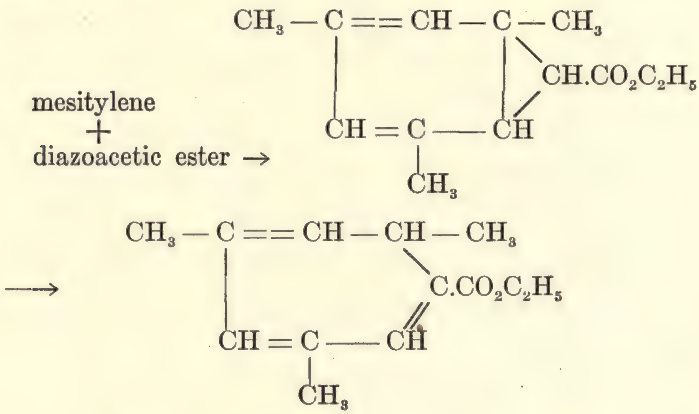
Cinnamic aldehyde yields phenylcyclopropane and phorone yields a dimethylisobutenylcyclopropane. This synthesis, discovered by Kishner, is another example, illustrating the remarkable reactivity of the group $-CH=CH-CO-$.

As noted above cyclopropane derivatives are formed by the reaction of diazoacetic ester and olefine bonds, a reaction employed by Buchner to throw light on the constitution of camphene.[19]

[18] *J. Russ. Phys.-Chem. Soc. 45*, 987 (1913); *J. Chem. Soc. Abs. 1913*, I, 1163, 1165.
[19] *Ber. 46*, 759 (1913).



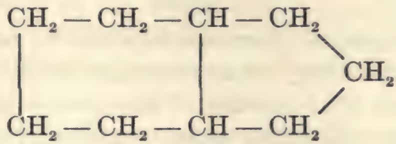
The formation of a seven carbon ring from a cyclohexane derivative has been noted in the reaction of mesitylene and diazoacetic ester, the intermediate product being smoothly decomposed in the presence of copper powder at 105°. This is another illustration of rearrangement which undoubtedly takes place through the intermediate formation of a cyclopropane derivative.[20]



The formation of cyclic non-benzenoid hydrocarbons by hydrogenation of aromatic hydrocarbons is a useful method for the preparation of a limited number of substances and these could very properly be given the appellation hydroaromatic compounds. The hydrogenation of benzene at 180°–200° over finely divided nickel was first carried out in 1901 by Sabatier and Senderens,[21] and cyclohexane made in this way has been employed to some extent as a motor fuel for aeroplanes.[22] On hydrogenating naphthalene, tetrahydronaphthalene is the principal product at 180°–200°, but at 250° and 120° atmospheres pressure decahydronaphthalene is formed. Tetrahydronaphthalene has recently become an industrial product, being recommended as a solvent or tur-

[20] Buchner, *Ber.* *53*, 865 (1920).
[21] *Compt. rend.* *132*, 210 (1901).
[22] *Cf.* Brit. Pat. 133,288; 133,667 (1919).

pentine substitute.[23] The xylenes readily yield the corresponding dimethylcyclohexane, p-cymene is converted into para-menthane, and meta-menthane is easily obtained by the catalytic hydrogenation of sylvestrene.[24] Indene at 250° and under pressure may be hydrogenated to octahydrindene or bicyclononane.[25]



Dibenzyl ketone, made from phenylacetic acid, yields dicyclohexylpropane on hydrogenation by catalytic nickel and hydrogen.

Cyclic Non-benzenoid Hydrocarbons.

As pointed out in the preface, it is difficult to classify the non-benzenoid hydrocarbons in a way which will not unduly emphasize slight differences in chemical behavior or structure. As regards chemical behavior we should certainly consider cyclopentane with normal pentane and cyclohexane with normal hexane. Also, the amount of information dealing with the derivatives of cyclohexane exceeds the sum total of that dealing with all the other cyclic non-benzenoid hydrocarbons. The reasons for this are the long standing interest in the chemistry of benzene, the conversion of benzene and a few of its derivatives to cyclohexane derivatives by hydrogenation, and the availability of material for investigation, as in the case of the terpenes. Practically all of the other cyclic non-benzenoid hydrocarbons have been obtained only by synthesis, only a very few of the simplest of such hydrocarbons having been isolated from petroleum. Although the quantity of information regarding cyclohexane is so relatively large, the use of the term "hydroaromatic" for the cyclohexane series is very unfortunate and will be avoided in the following pages as much as possible.

Some writers may consider that cyclopropane may properly be considered together with ethylene and its derivatives but the so-called un-

[23] Cf. Tetralin and Similar Hydrogenated Products,—Frydlender, *Rev. prod. chim.* *23*, 719 (1920).

[24] Sabatier & Marat, *Compt. rend.* *156*, 184 (1913).

[25] Ipatiev, *J. Chem. Soc. Abs.* *1913*, I, 1165; Osterberg & Kendall, *J. Am. Chem. Soc.* *42*, 2616 (1920), recommend Ipatiev's method for the preparation of cyclohexane from benzene. The method consists simply in placing the benzene and catalyst in a tight bomb, heating to 250° and passing in hydrogen at 1800 lbs. pressure from a pressure cylinder.

saturation of cyclobutane places it close to cyclopropane and in a position intermediate between cyclopentane and cyclopropane. However, some concession must be made to the necessity of some sort of orderly arrangement of subject matter and the writer has elected to discuss the cyclic non-benzoid hydrocarbons in a series beginning with cyclopropane.

There are two general classes of information regarding the cycloparaffines and particularly the cyclohexane series. On the one hand there is a relatively large amount of information obtained by the investigation of pure substances, either synthesized or isolated from a natural product as is usually the case in the study of the terpenes; this information is usually accurate and satisfactory, from a scientific point of view. The second type of information is much less definite and less reliable and has to do with very imperfectly known mixtures such as petroleum distillates, shale oils, rosin oils, and similar products whose literature is nevertheless considerable by reason of their commercial importance. In dealing with the chemistry of these substances the scientific and industrial works have usually been rigidly exclusive, each of the other class of information. However, the proportion of information of permanent scientific value contributed by the industries is becoming greater than ever before and cannot be passed by, and in the following pages information from industrial sources will be included whenever it is of interest and appears to be of permanent scientific value.

Cyclopropanes: Simple cyclopropane hydrocarbons have not been found in nature but the bicyclic terpenes sabinene and carene possess three carbon rings, as does also the ketone thujone. The similarity of the cyclopropane ring to the ethylene bond has repeatedly been pointed out. Its influence upon physical properties is less marked than in the case of the double bond, as has been reviewed in the section on physical properties. Carr and Burt [26] conclude, from a study of absorption spectra, that the cyclopropane ring is a "center of residual affinity" similar in character but intermediate in quantity to that of the double bond, and as such can form a conjugated system with the carbonyl group. The relative stability of the derivatives of cyclopropane varies within wide limits, with different substituent groups, as will be brought out in the following pages.

Kohler and his students have shown, in a series of papers, that substituents have exactly the same effect upon the mode of addition to a

[26] *J. Am. Chem. Soc.* **40**, 1590 (1918).

cyclopropane ring as to an ethylene linkage, even though the saturated open-chained compounds formed in the two cases are quite different in structure.[27] Thus, as pointed out by Kohler and Conant, the mode of addition of hydrobromic acid to cyclopropane hydrocarbons is determined by the number and arrangement of the alkyl groups. The ring invariably opens between the carbon atoms that hold the largest and the smallest number of alkyl groups and the principal product is always one in which the halogen is combined with the carbon atom that holds the largest number of alkyl groups. In the case of cyclopropane carboxylic acids the CO_2H groups may affect the ease with which addition takes place, but the product is always either a γ-bromo acid or the corresponding lactone. The few ketones that have been studied behave like the acids. In cases where a carbonyl group is next to the ring the halogen atom accordingly always goes to the β-position in the ring, for example,

$$\begin{array}{l} CH_2 \\ | \quad >CH.CO_2H + HBr \longrightarrow CH_2Br.CH_2CH_2.CO_2H \\ CH_2 \end{array}$$

$$\begin{array}{l} CH_2 \\ | \quad >CH.CO.C_6H_5 + HBr \longrightarrow CH_2Br.CH_2CH_2COC_6H_5 \\ CH_2 \end{array}$$

Kohler and his assistants find that derivatives of the type

$$\begin{array}{c} C_6H_5CH - CH.COC_6H_5 \\ \diagdown \;\; \diagup \\ C(CO_2R)_2 \end{array}$$

are quite stable to cold permanganate solution and to ozone but are hydrolyzed by water with "unusual rapidity," and, in the absence of water, alcoholates, ammonia and amines rapidly convert them into isomeric unsaturated compounds.

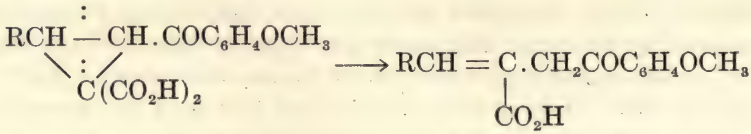
The cyclopropane ring may be broken in different ways depending upon the conditions and the reaction employed. The phenylanisoyl derivative studied by Miss Hahn[28] breaks down in the three ways indicated below,

(1) With alkali alcoholates

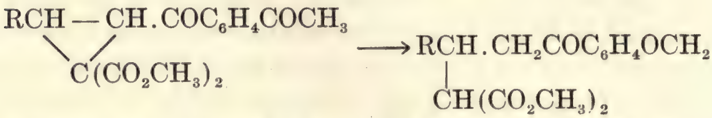
$$\begin{array}{c} C_6H_5CH - CH.COC_6H_4OCH_3 \\ \diagdown \;\; \diagup \\ C(CO_2CH_3)_2 \end{array} \longrightarrow \begin{array}{l} C_6H_5CH = C - COC_6H_4OCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad CH(CO_2CH_3)_2 \end{array}$$

[27] Cf. Kohler & Conant, *J. Am. Chem. Soc.* *39*, 1404 (1917).
[28] *J. Am. Chem. Soc.* *38*, 1520 (1916).

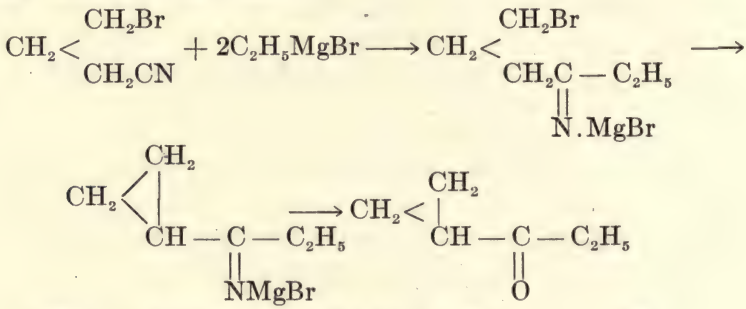
(2) When the dibasic acid is heated CO_2 is evolved accompanied by rupture of the ring,

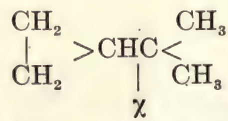


(3) When the ester in solution in acetic acid is reduced with zinc dust the reduced derivate is obtained

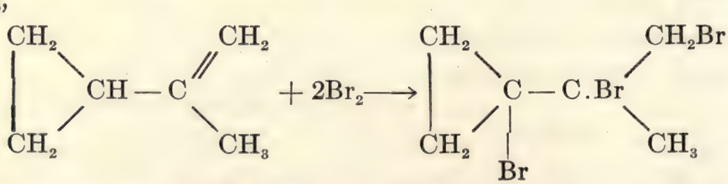


A series of cyclopropane derivatives has been made by Bruylants [29] starting with the novel reaction,



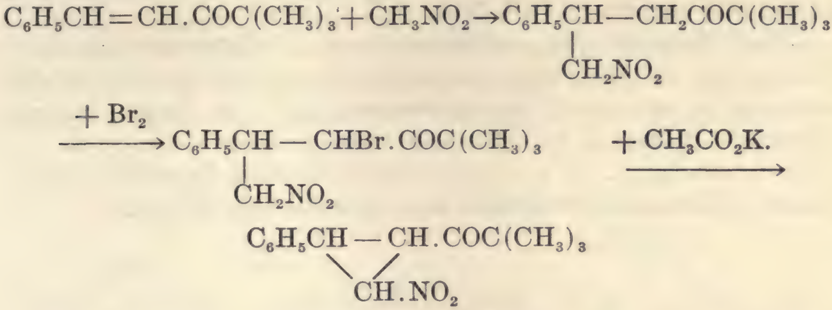
Halogen derivatives of the type 

are quite stable to boiling aqueous caustic alkali but boiling with alcoholic alkali gives a mixture of the ether and the unsaturated hydrocarbon. When the unsaturated hydrocarbon is treated with bromine a tribromide is formed, the double bond taking up Br_2 and the tertiary hydrogen atom being replaced *without* rupture of the cyclopropane ring,



[29] *Rec. trav. chim.* **28**, 180 (1909).

Kohler has made a number of nitro derivatives of cyclopropane by reacting upon unsaturated substances with nitromethane, brominating and removing HBr, for example,[30]



Cyclopropane is reduced to propane by hydrogen and catalytic nickel slowly at 80° and rapidly at 120°, but cyclobutane requires a temperature of approximately 180° for hydrogenation to butane.[31] Cyclopropane thus occupies a position intermediate in stability, to hydrogen and nickel, between cyclobutane and ethylene, the latter being reduced to ethane at temperatures as low as —15°. Cyclopropane is readily reduced to propane by colloidal platinum in acetic acid but cyclopropane-1.1-dicarboxylic acid is not reduced under these conditions.[32] Ethylene is reduced a little more rapidly than cyclopropane by this method (Fokin-Willstätter method).

In contact with iron conversion of cyclopropane to propylene[33] can be observed at 100°, but in the presence of platinum black the reaction is slow at 200°, although rapid at 315°.

Cyclopropane can be prepared[34] by the reduction of 1.3-dibromopropane by zinc in alcohol (75 per cent) at temperatures not exceeding 60°. It was first made by the action of sodium on this dibromide. It is thus evolved as a gas, easily condensed to a liquid boiling at —35° (749 mm.).

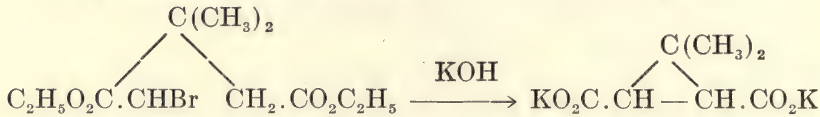
Methyl Cyclopropane,[35] boiling-point 4° to 5°, is formed when 1.3-dibromobutane is treated with zinc dust in alcohol, in the same manner in which Gustavson prepared cyclopropane from 1.3-dibromopropane.

1.1-Dimethylcyclopropane,[36] boiling-point 21°, like other deriva-

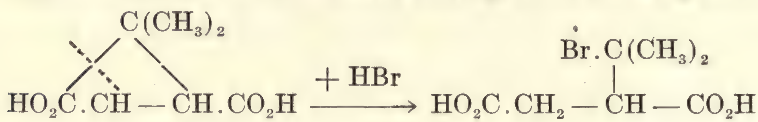
[30] Kohler & Rao, *J. Am. Chem. Soc. 41*, 1697 (1919).
[31] Willstätter & Bruce, *Ber. 40*, 4459 (1907).
[32] Boeseken and others, *Rec. trav. chim. 35*, 260 (1916).
[33] Ipatiev, *Ber. 35*, 1057 (1902); *36*, 2014 (1903).
[34] Gustavson, *J. prakt. Chem.* (2) *76*, 512 (1907).
[35] Demjanoff, *Ber. 28*, 22 (1895).
[36] Ipatiev & Huhn, *Ber. 36*, 2014 (1903).

tives of cyclopropane, reacts only very slowly with permanganate, and may thus be distinguished from the isomer trimethylethylene, the latter hydrocarbon being formed when 1.1-dimethylcyclopropane is passed over alumina at 340°–345°.

The 2.3-dicarboxylic acid derivative of 1.1-dimethylcyclopropane is of interest as having been produced by Baeyer and Ipatiev [37] by the oxidation of carone and later synthesized by W. H. Perkin, Jr., and Thorpe.[38] It exists in two physically isomeric forms known as *cis* and *trans*-caronic acids. It was synthesized by treating the ester of monobromo-ββ-dimethylglutaric acid with alcoholic caustic potash.



Hydrobromic acid at 100° breaks the ring in the following manner:



The alkali salts of cis and trans-caronic acids are quite stable to aqueous permanganate.

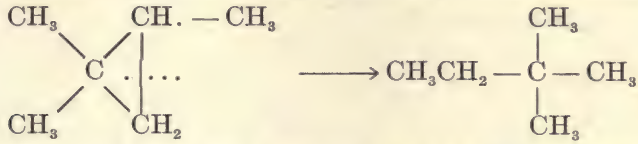
1.2.-Dimethylcyclopropane has been made from 2.4-dibromopentane by Gustavson's method. It boils at 32°–33°, d $\frac{0°}{4°}$ 0.7025, d $\frac{20°}{4°}$ 0.6806, n $\frac{10°}{D}$ 1.3823.

1.2.3.-Trimethylcyclopropane was made by first synthesizing 3-methylpentanediol-(2.4). This was converted to the corresponding dibromide by heating with hydrobromic acid and the dibromide treated with zinc dust in 80 per cent alcohol, yielding the hydrocarbon, boiling-point 65°–66°, d $\frac{22°}{4°}$, 0.6921, n $\frac{22°}{D}$ 1.3942. It is quite stable to aqueous permanganate.

1.1.2.-Trimethylcyclopropane was made by Kishner [39] from mesityl oxide by his hydrazine method. The hydrocarbon boils at 52.8° d $\frac{20°}{0°}$ 0.6949, n_D 1.3866. It is easily dissolved by nitric acid (1.52) and reacts with concentrated sulfuric acid giving a mixture of kero-

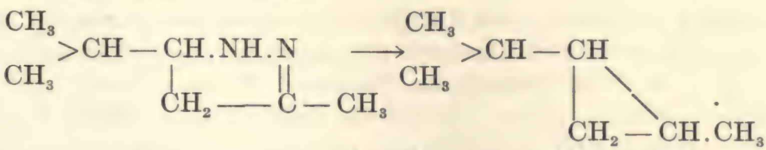
[37] *Ber.* *29,* 2796 (1896).
[38] *J. Chem. Soc.* *75,* 48 (1899).
[39] *J. Russ. Phys.-Chem. Soc.* *44,* 165 (1912)

sene-like hydrocarbons boiling mostly within the range 170°–360°. These higher boiling hydrocarbons are probably formed by the intermediate formation of an olefine followed by polymerization in accordance with the general behavior of olefines to concentrated sulfuric acid which has been discussed elsewhere in these pages. With nitric acid in glacial acetic acid hydration occurs, resulting chiefly in isopropyl dimethyl carbinol. It is reduced by Sabatier's method as follows:



Fuming hydroiodic acid and bromine break the cyclopropane ring.

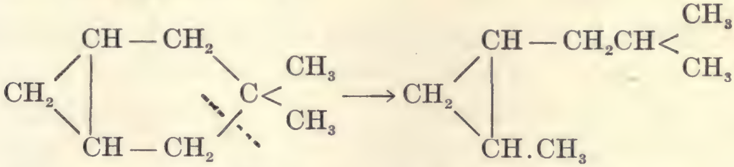
Methylisopropylcyclopropane is formed by heating methyl isopropyl pyrazoline (from isobutylidene-acetone and hydrazine hydrate) to 230° with caustic potash.[40]



The hydrocarbon boils at 80°–81°, d $\frac{20°}{0°}$ 0.7120, n $\frac{20°}{D}$ 1.3927.

1-Methyl-1.2.-Diethylcyclopropane has been made by Kishner's hydrazine method. It boils at 108°–109°, d $\frac{20°}{0°}$ 0.7382, n_D 1.4102. It is markedly more stable to permanganate solution than 1.1.2.-trimethylcyclopropane and is also less reactive to bromine.[41]

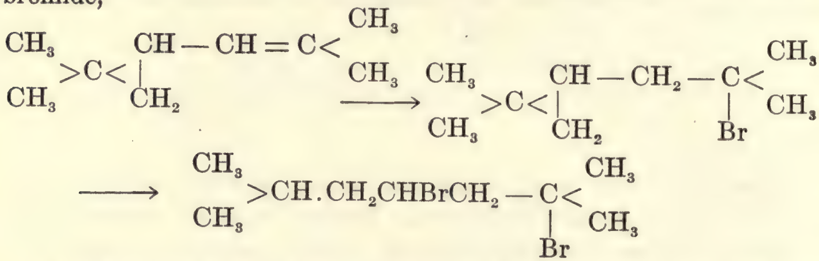
Methylisobutylcyclopropane was made by Zelinsky [42] by hydrogenating the dimethylbicyclohexane, shown below, in the presence of platinum or palladium black,



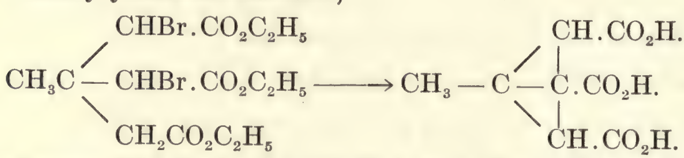
It boils at 110°–111°, d $\frac{20°}{4°}$ 0.7403. In the presence of nickel and hydrogen the cyclopropane ring is also broken and reduced.

[40] Kishner, *J. Russ. Phys.-Chem. Soc.* *45*, 987 (1913).
[41] Kishner, *J. Russ. Phys.-Chem. Soc.* *44*, 165 (1912).
[42] *J. Russ.* *45*, 831 (1913).

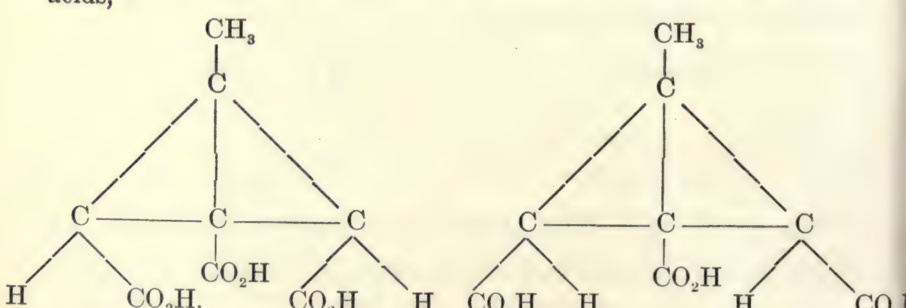
1.1.-Dimethyl-2-Isobutenylcyclopropane is formed when phorone is heated with hydrazine hydrate; boiling-point 132°, $d\frac{20°}{0°}$ 0.7677, n_D 1.442.[43] It may be oxidized to 1.1.-dimethylcyclopropanecarboxylic acid by means of permanganate without rupture of the ring. Treatment with fuming HBr gives first the monobromide and then the dibromide,



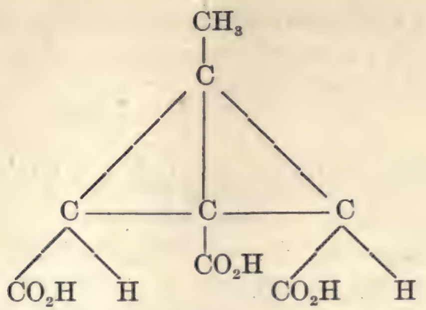
A tricarboxylic acid derivative of methyl dicyclobutane has been prepared by Beesley and Thorpe[44] and is mentioned because of its curious structure, its method of preparation and the fact that it exists in three distinct modifications, in accord with accepted ideas of stereochemistry. When the dibromoethyl ester of the acid $CH_3C.(CH_2CO_2H)_3$ is treated with pyridine a dilactone ester is formed which readily yields the free acid,



Three distinct modifications melting at 193°, 165° and 154° were isolated, which evidently correspond to the three theoretically possible acids,



[43] Kishner, *J. Russ. Phys.-Chem. Soc.* 45, 957 (1913).
[44] *J. Chem. Soc.* 117, 601 (1920).



These acids are remarkably stable and are not affected by prolonged boiling with aqueous acids or alkalies.

Cyclobutane: This hydrocarbon, boiling-point 11°–12°, D_4° 0.7038, is readily made by hydrogenating cyclobutene in the presence of nickel at 100°. Hydrogen in the presence of nickel, at 180°, converts cyclobutane to normal butane. It is stable at ordinary temperatures to bromine and hydriodic acid. Its simple derivatives show a striking resemblance in physical and chemical properties to the derivatives of n.butane. Thus cyclobutanol $\begin{array}{l} CH_2 - CHOH \\ | \qquad\quad | \\ CH_2 - CH_2 \end{array}$ and n.butyl alcohol are very similar in odor and boiling-point, 123° and 116.8° respectively. W. H. Perkin, Jr.,[45] who prepared cyclobutanol, stated, "It shows the closest resemblance to the fatty alcohols containing the same number of carbon atoms; it might, indeed, be readily mistaken for normal butyl alcohol." Perkin also found that cyclobutylcarboxylic acid behaves very much like valeric acid, the amide giving excellent yields of the amine, with bromine and caustic potash.

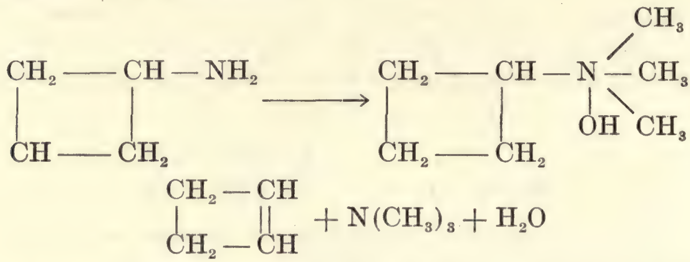
$$\begin{array}{l} CH_2 - CH.CONH_2 \\ | \qquad\quad | \\ CH_2 - CH_2 \end{array} \qquad\qquad \begin{array}{l} CH_2 - CHNH_2 \\ | \qquad\quad | \\ CH_2 - CH_2 \end{array}$$

The cyclobutane derivatives all have slightly higher boiling-points than the corresponding normal butane derivatives.

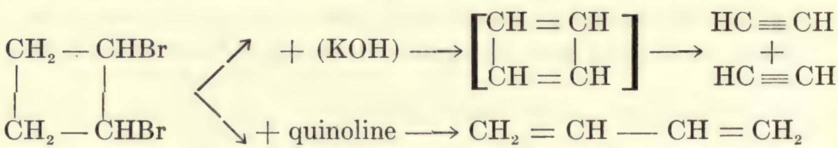
Cyclobutyl Series		*Normal Butyl*		
Substance	*B.-P.*	*Substance*	*B.-P.*	*Diff.*
$R.CO_2H$	195°	R_1CO_2H	186°	9°
$R.NH_2$	81°	R_1NH_2	76°	5°
R.OH	123°	R_1OH	116°	7°
R.Cl	85°	R_1Cl	77°	8°
RBr	104°	R_1Br	100°	4°
RI	138°	R_1I	131°	7°

[45] *J. Chem. Soc. 65*, 950 (1894).

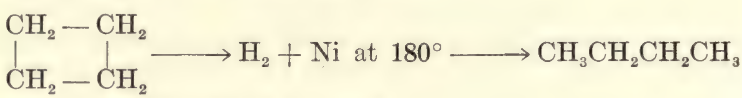
Willstätter [46] and his co-workers have applied the well-known method of exhaustive methylation and decomposition of the tertiary base, to the preparation of cyclobutene.

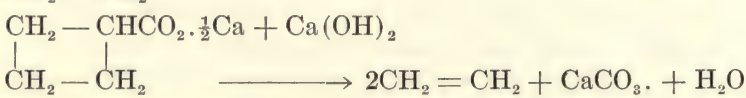


Cyclobutene readily adds one molecule of bromine to form the comparatively stable dibromide boiling-point 171°–174°. When heated with quinoline this dibromide decomposes with rupture of the ring, giving butadiene but with caustic potash at 200° acetylene is formed.[47]



The following methods of rupturing the ring of cyclobutane or its simple derivatives have been observed.

(1) 

(2) 

heat

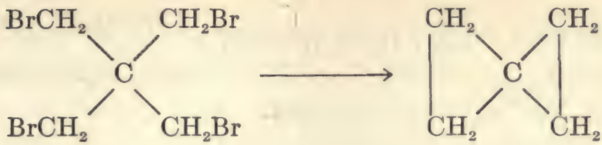
(3) 1.2-dibromocyclobutane + quinoline ⟶ butadiene.

(4) Cyclobutylamine phosphate + heat ⟶ butadiene.

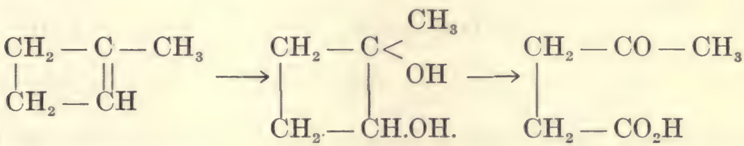
(5) 1.2-dibromocyclobutane + KOH ⟶ acetylene.

Gustavson [48] prepared a hydrocarbon C_5H_8 by the action of zinc in alcohol on $C(CH_2Br)_4$ and from the manner of its formation and its physical properties and chemical behavior Gustavson's hydrocarbon has been considered to be spirocyclane,

[46] *Ber.* *38*, 1992 (1905); *40*, 3979 (1907).
[47] The 1.3-diphenyl derivative of cyclobutadiene is a stable crystalline hydrocarbon melting at 130°. [Gastaldi & Cherchi, *Gazz. chim. Ital.* *44* (1), 282.]
[48] *J. prakt. Chem.* (2) *54*, 105 (1896); *56*, 93 (1897).

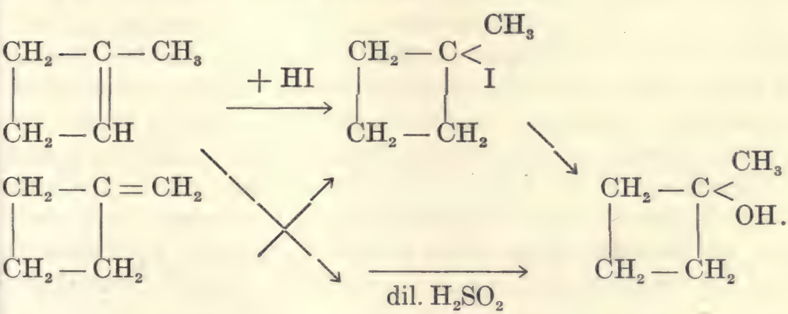


However, it has been shown that by careful fractional distillation Gustavson's product may be separated into two hydrocarbons, one boiling at 37.5° and the other at 42°. Philipow [49] has demonstrated that both hydrocarbons are derivatives of cyclobutane, the lower boiling one yielding levulinic acid on oxidation,



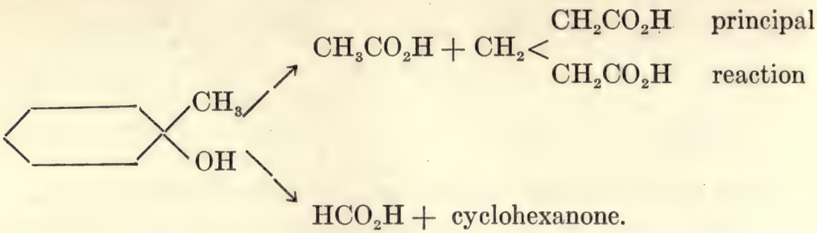
methylcyclobutene

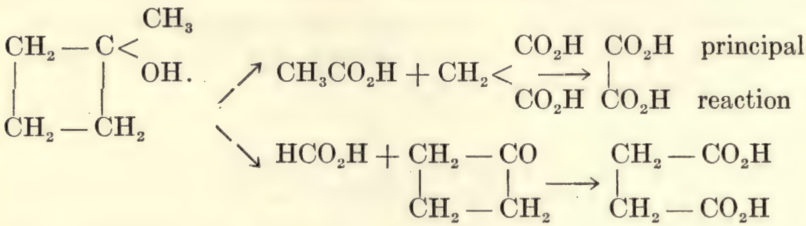
The hydrocarbon boiling at 42° proved to be methenecyclobutane. Both hydrocarbons yield the same hydroiodide and treatment of this iodide with moist silver oxide yields an alcohol boiling at 116°–119°. The same alcohol is obtained directly from both hydrocarbons by careful hydration by dilute sulfuric acid,



Previous results on the oxidation of the hydrocarbon boiling at 42° and the alcohol had led to no very definite results, but Philipow showed that the oxidation of the alcohol is strictly analogous to the oxidation of 1-methylcyclohexanol (1),

[49] *J. prakt. Chem.* (2) 93, 162 (1916).





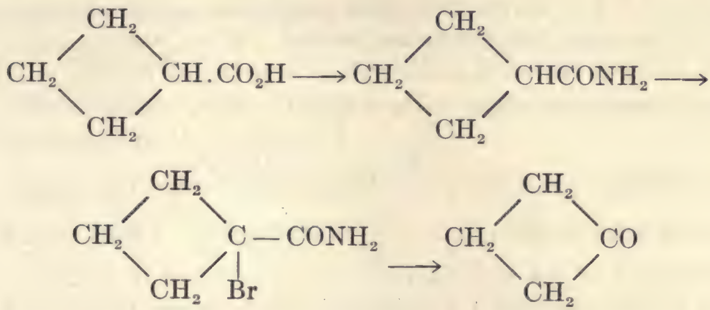
Hydrogenation had yielded a hydrocarbon C_5H_{10}, supposed, on the basis of the spirocyclane structure, to be ethylcyclopropane. Philipow made ethylcyclopropane [50] by Kishner's admirable method, from acetylcyclopropane,

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CH.CO.CH_3 + H_2N.NH_2 \rightarrow \begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CH.CH_2CH_3 + N_2 + H_2O$$

Perkin and Colman [51] had stated that methylcyclobutane was produced by the action of sodium, in toluene, on 1.4-dibromopentane but on repeating their work Philipow obtained a similar product but showed that it was a mixture of hydrocarbons, in which he identified piperylene and n.pentene. Demjanow [52] had made methylcyclobutane by the action of zinc in acetic acid on cyclobutylmethyl iodide. Philipow made this hydrocarbon in two ways, from cyclobutylaldehyde $C_4H_7.CHO$ by Kishner's method, and also by reduction of Gustavson's hydrocarbons by colloidal palladium (Skita's method), and the hydrocarbon obtained by the three methods proves to be identical, i. e., methylcyclobutane, boiling-point 36°–36.5° (755 mm.), $d\frac{0°}{4°}$ 0.7118, MR 23.58, MR calc. 23.02. Methylcyclobutane reacts with hydrogen in the presence of catalytic nickel at 205° to give isopentane.

[50] Philipow's ethylcyclopropane boils at 36.5° (755mm.), $d\frac{0°}{4°}$ 0.7055, MR 23.61, MR calculated 23.02.
[51] *J. Chem. Soc. 53,* 201 (1888).
[52] *J. Russ. Phys.-Chem. Soc. 42,* 842 (1910).

Cyclobutanone, boiling-point 99°–101°, $d\frac{18°}{18°}$ 0.9344, has an odor resembling acetone. Oxidation by nitric acid yields succinic acid. It was made by Kishner from cyclobutanecarboxylic acid by treating with ammonia to form the amide, brominating and then treating with bromine and caustic potash,



Cyclobutene is of interest on account of the series of bromine substitution products which can be prepared from it without rupture of the ring. Thus cyclobutene adds a molecule of bromine to form 1.2-dibromocyclobutane. On treating this with alkali one molecule of hydrogen bromide is removed and the resulting bromocyclobutene, like aliphatic olefines containing halogen, is relatively quite stable. It adds HBr to form 1.1-dibromocyclobutane which on hydrolyzing with aqueous lead oxide yields cyclobutanone. Bromocyclobutene adds bromine to form 1.1.2-tribromocyclobutane, which can be converted to

$$\begin{array}{ccc} CH_2 & — & CBr \\ | & & \| \\ CH_2 & — & CBr \end{array}$$

by loss of HBr, and this in turn adds bromine to give

$$\begin{array}{ccc} CH_2 & — & CBr_2 \\ | & & | \\ CH_2 & — & CBr_2 \end{array}$$

melting-point 126° and this can be further brominated without breaking the ring to form pentabromocyclobutane, and hexabromocyclobutane melting at 186.5°.[53]

Ethylcyclobutane has been prepared by a very roundabout method from the amide of cyclobutanecarboxylic acid, which was converted into cyclobutylmethyl ketone, this reduced to cyclobutylmethylcarbinol and the latter converted to the corresponding iodide and reduced by zinc dust and acetic acid.[54] The hydrocarbon boils at 72.2°–72.5°,

[53] Willstätter & Bruce, *Ber.* *40*, 3979 (1908).
[54] Zelinsky & Gutt, *Ber.* *34*, 2432 (1908).

$d\frac{10°}{4°}$ 0.7540, $d\frac{20°}{4°}$ 0.7450 and $n\frac{19.5°}{D}$ 1.4080. Oxidation by nitric acid yields succinic acid. Cyclobutylmethyl ketone boils at 136°–136.5° (semicarbazone melting at 148°) and the cyclobutylmethylcarbinol $C_4H_7.CHOH.CH_3$, boils at 144° (phenylurethane melting at 87.5°–88°).

Lebedev[55] has shown that when substituted allenes are polymerized, cyclobutane derivatives are formed. When unsymmetrical dimethyl allene is heated in sealed tubes the principal product is *1.2-diisopropylidenecyclobutane*

$$\begin{array}{l} CH_2 - C = C(CH_3)_2 \\ | \qquad\quad | \\ CH_2 - C = C(CH_3)_2 \end{array}$$

together with 1.1-dimethyl-2-methylene-3-isopropylidenecyclobutane. The former hydrocarbon boils at 179°–181°, $d\frac{20°}{4°}$ 0.8422, $n\frac{19.7°}{D}$ 1.5008 from which the increment of the molecular refraction is shown to be 2.32. It is readily hydrogenated to 1.2-diisopropyl-cyclobutane, boiling at 157°–158.5°, $d\frac{0°}{4°}$ 0.7901. The monoözonide yields isopropylidene-2-cyclobutanone,

$$\begin{array}{l} CH_2 - C = O \\ | \qquad\quad | \\ CH_2 - C = C(CH_3)_2 \end{array}$$

boiling-point 171°. Isopropyl-2-cyclobutanone obtained by reduction, boils at 148°–150° (semicarbazone melting at 183°).

The hydrocarbon *1.1-dimethyl-2-methylene-3-isopropylidene* boils at 149°–150°, $d\frac{20°}{4°}$ 0.7982. The corresponding saturated hydrocarbon obtained by reduction, i. e.,—1.1.2-trimethyl-3-*isopropylcyclobutane,* boils at 145°–146°, $d\frac{20°}{4°}$ 0.7598. The two unsaturated hydrocarbons have a sharp kerosene-like odor. The two saturated hydrocarbons are not attacked by aqueous permanganate. The stability of the saturated cyclobutanes to sulfuric acid has not been noted.

Cyclobutane-1.1-Dicarboxylic Acid, melting-point 155°, is prepared by a general method discovered by Perkin, i. e.,—the reaction of 1.3-dibromopropane and sodium malonic acid ester or sodium cyanacetic ester.

$$CH_2<\begin{matrix} CH_2Br \\ CH_2Br \end{matrix} + 2Na + H_2C<\begin{matrix} CO_2R \\ CN \end{matrix} \longrightarrow CH_2<\begin{matrix} CH_2 \\ CH_2 \end{matrix}>C<\begin{matrix} CO_2H \\ CO_2H \end{matrix}$$

Decomposition of the dicarboxylic acid yields,

[55] *J. Russ. Phys.-Chem. Soc.* 43, 820 (1911).

Cyclobutanecarboxylic Acid, boiling-point 194°. The acids of this type resemble fatty acids very closely, this acid readily yielding a pleasant smelling ethyl ester boiling at 160°, an anhydride boiling at 160°, an amide melting at 130° and a nitrile boiling at 150°. Hydriodic acid at 200° breaks the ring forming n.valeric acid.[56] When the silver salt is treated with iodine, a peculiar condensation with formation of the ester of cyclobutanol results,[57]

$$2C_4H_7CO_2Ag + I_2 \longrightarrow C_4H_7CO_2.C_4H_7 + CO_2 + 2AgI$$

Cyclobutane 1.1.2.2.-Tetracarboxylic Acid, melting-point 145°–150° is formed by the reaction

$$\begin{array}{l} CH_2-CNa<\begin{matrix}CO_2R\\CO_2R\end{matrix} \\ | \\ CH_2-CNa<\begin{matrix}CO_2R\\CO_2R\end{matrix} \end{array} \xrightarrow[\text{or } I_2]{Br_2} \begin{array}{l} CH_2-C<\begin{matrix}CO_2R\\CO_2R\end{matrix} \\ |\qquad\;\; | \\ CH_2-C<\begin{matrix}CO_2R\\CO_2R\end{matrix} \end{array}$$

On heating the free acid it loses two molecules of carbon dioxide and forms *cyclobutane-1-2-dicarboxylic acid,* melting at 137°, known in *cis* and *trans* forms. On brominating the 1.2-dibromide is formed. By the action of caustic alkalies one molecule of HBr is removed to form the bromocyclobutene carboxylic acid,

$$\begin{array}{l} CH_2-CBr-CO_2H. \\ |\qquad\;\; | \\ CH_2-CBr-CO_2H. \end{array} \xrightarrow{KOH} \begin{array}{l} CH_2-CBr \\ |\qquad\;\; \| \\ CH_2-C.CO_2H \end{array} + CO_2 + HBr$$

Silver oxide in water replaces both bromine atoms with hydroxyl, these reactions being quite analogous to the formation of bromofumaric acid and tartaric acid from isodibromosuccinic acid under the same conditions,

$$\begin{array}{l} CHBr.CO_2H. \\ | \\ CHBr.CO_2H \end{array} \longrightarrow \begin{array}{l} CH-CO_2H \\ \| \\ CBr-CO_2H \end{array} \text{ and } \begin{array}{l} CH(OH).CO_2H \\ | \\ CH(OH).CO_2H. \end{array}$$

Cyclobutane -1.3-Dicarboxylic Acid is known in *cis* and *trans* forms, melting at 136° and 171°, respectively. Simonsen[58] has shown that when the ethyl ester of β-methoxymethylmalonic acid is digested

[56] Kishner, *J. Russ. Phys.-Chem. Soc.* *40,* 673 (1908).
[57] Demjanov, *J. Russ. Phys.-Chem. Soc.* *43,* 835 (1911).
[58] *J. Chem. Soc.* *93,* 1778 (1908).

with hydrochloric acid it yields *cis*-cyclobutane-1.3-dicarboxylic acid.

The cyclobutane ring exists in α-truxillic acid, which, according to De Jong,[59] is 1.3-diphenyl-cyclobutane-2.4-dicarboxylic acid. It is formed from cinnamic acid by the action of light and on heating breaks up again into cinnamic acid.

Cyclopentane: The relationship between cyclopentane and cyclohexane, or their derivatives, is exceedingly close, and the increasing number of instances known, in which change of the one ring system into the other occurs, makes evident the rationality and convenience of considering these two ring systems together, rather than isolating the cyclohexane derivatives as "hydroaromatic" compounds, as has usually been done heretofore and thus widely separating the subject matter dealing with these two ring systems. Examples of the conversion of these two ring systems, one into the other, have been noted in the section on *Rearrangements.* Thus one of the smoothest reactions of this kind is the nearly quantitative conversion of 1-methyl-1-α-hydroxyethylcyclopentane to 1.2-dimethyl-Δ^1-cyclohexene by zinc chloride.[60] Cyclopentane is also formed when the bromide of cyclobutylcarbinol is reduced by the zinc-palladium couple and hydrobromic acid.[61] Kishner showed that when benzene is reduced under high pressure at 280°, according to Wreden, that the product is not cyclohexane but methylcyclopentane[62] and Markownikow[63] has shown several instances in which benzene hydrocarbons give cyclopentane derivatives on hydrogenation. Cyclohexanol yields chiefly methylcyclopentane on heating with concentrated hydriodic acid. The hydrocarbons themselves are quite stable; only in reactions of their derivatives does rearrangement of the ring structure occur easily. Thus Markownikow and Fortey[64] independently observed that cyclohexane could be heated with hydriodic acid (and red phosphorus) in sealed tubes to 240° without change. Methylcyclohexane is, however, partially rearranged by heating with hydriodic acid to 270° to dimethylcyclopentane, and this change is effected without the formation of higher boiling products, in other words, is not a thoroughgoing decomposition such as occurs in "cracking" processes. Methylcyclopentane is one of the products of the action of aluminum chloride on cyclohexane.[65]

[59] *Chem. Abs. 1918,* 1385; Stoermer & Laage, *Ber. 54,* 77 (1921).
[60] Meerwein, *Ann. 417,* 255 (1918).
[61] Demjanow, *Ber. 40,* 4960 (1907).
[62] *J. Russ. Phys.-Chem. Soc. 29,* 210 (1897).
[63] *Ber. 30,* 1214 (1897).
[64] *Proc. Chem. Soc. 1897,* 161.
[65] Aschan, *Ann. 324,* 12 (1902).

Cyclopentane was prepared by Wislicenus [66] from cyclopentanone, the latter being prepared by the well-known method of heating calcium adipate. Cyclopentanone is also a constituent of the oily residues recovered in the rectification of wood alcohol. The ketone on reduction under the same conditions usually applied to ordinary aliphatic ketones, for example, reduction by means of sodium in moist ether, yields cyclopentanol. The alcohol has an odor resembling amyl alcohol, boils at 139°, d $\frac{21.5°}{4°}$ 0.9395. Cyclopentanol is converted into the corresponding iodide by saturating with hydrogen iodide and hydrogen bromide yields the bromide, without rupture of the ring. Reduction of the iodide under the usual conditions, zinc and hydrochloric acid in dilute alcohol, yields *cyclopentane,* boiling-point 50.5°–50.7°, d $\frac{20.5°}{4°}$ 0.7506.

Cyclopentane is inert to bromine in the dark but in sunlight substitution with evolution of HBr occurs, approximately with the same ease as in the case of normal pentane. On heating with bromine in a sealed tube the reaction is very slow at 100° but more rapid at 128°–130°, the reaction then being accompanied by deposition of carbon.

Cyclopentane has not been sulfonated, the hydrocarbon being quite stable to sulfuric acid. Borsche [67] has prepared cyclopentane sulfonic acid by an indirect method involving the conversion of cyclopentanol to the bromide, reacting on the bromide with magnesium in ether and treating the magnesium complex C_5H_9MgBr with SO_2 and then oxidizing with aqueous permanganate. The potassium cyclopentyl sulfonate was crystallized from absolute alcohol. Salts of methylcyclohexane-3-sulfonate were prepared in the same manner from 1 methyl-3-bromocyclohexane.

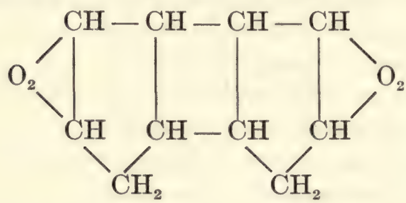
Cyclopentene is readily formed on warming cyclopentyl iodide with alcoholic caustic potash, closely resembling amyl iodide and its conversion to amylene under the same conditions. Cyclopentene boils at 46°. When cyclopentyl bromide is employed a small proportion of cyclopentyl ethyl ether is also formed, again paralleling the n.amyl derivatives. From cyclopentene Meiser [68] prepared the dibromide, which he converted to the 1.2-glycol by hydrolyzing with aqueous potassium carbonate; the glycol was converted to the chlorohydrin by

[66] *Ann.* 275, 327 (1893).
[67] *Ber.* 40, 2220 (1907). Borsche prepared 1-methyl-cyclohexane-3-sulfone-chloride, which on reduction yields the 1-methyl cyclohexane-thiol (3), boiling at 172°,—the first of the cyclic mercaptans to be synthesized.
[68] *Ber.* 32, 2050 (1899).

hydrochloric acid and the same product was made by the addition of hypochlorous acid to cyclopentene.

In the cyclopentane series a very large number of derivatives are known, but the great majority of them have been synthesized by costly and usually very roundabout methods. The hydrocarbons themselves have seldom been used for preparing derivatives; in fact, the hydrocarbons have been prepared from the derivatives. Cyclopentane or its alkyl derivatives have never been isolated in a *pure* state from petroleum or any other natural product.

Cyclopentadiene, boiling-point 41°, may be isolated from the fore-runnings when crude benzene is distilled,[69] and Etard and Lambert[70] found it among the products of the thermal decomposition of heavy paraffine oil. It polymerizes spontaneously to the dimeride $C_{10}H_{12}$ on standing at ordinary temperatures and on distillation the dimeride is partially inverted to the original hydrocarbon. The dimeride (unknown constitution) boils at 170°. Stobbe[71] finds that the spontaneous conversion to the dimeride is complete in about 30 days and when exposed to oxygen or air a diperoxide of the dimeride is formed, which Stobbe regards as having the following structure,



The dimeride is much more stable than the original hydrocarbon but may be further polymerized by heating to 160°–180° in a sealed tube, a solid resin being formed.[72] The polymers of acyclic olefines and dienes are also more stable than the original hydrocarbons, the difference being marked in their behavior to concentrated sulfuric acid, hydrogen chloride, hydrogen bromide, etc. Hydrogen chloride combines with cyclopentadiene to form a monochlorocyclopentene, boiling-point 50° (40mm.), and this derivative, though not further acted upon by hydrogen chloride, combines readily with chlorine to form a trichlorocyclopentane boiling at 196°. Addition of bromine to cyclopentadiene gives two stereoisomeric 1.4-dibromides, one a liquid and

[69] Kraemer & Spilker, *Ber. 29,* 552 (1896).
[70] *Compt. rend. 112,* 945 (1891).
[71] *Ber. 52,* 1436 (1919).
[72] Kronstein, *Ber. 35,* 4150 (1902).

one a crystalline solid; the dibromides yield two stereo-isomeric αα-dibromoglutaric acids on oxidation. Cyclopentadiene, like isoprene, combines with quinones to give stable crystalline compounds; for example, with benzoquinone to form the product $C_{11}H_{10}O_2$, melting-point 78°. Cyclopentadiene reacts violently with concentrated sulfuric acid and dilute sulfuric acid resinifies it. Like cyclohexadiene, its polymers do not resemble caoutchouc but are resinous.

Cyclopentadiene is of special interest on account of the reactivity of the CH_2 group. The hydrocarbon reacts with potassium with evolution of hydrogen, forms C_5H_5MgI from CH_3MgI with evolution of methane [73] and readily condenses with aldehydes and ketones under the influence of sodium ethylate. Thiele [74] attributes this reactivity to the unsaturated character of the contiguous groups, its condensation with aldehydes and ketones paralleling the reactivity of substances containing the group $O = \overset{|}{C} - CH_2 - \overset{|}{C} = O$ with these reagents under the same conditions. With acetone, acetophenone, and benzophenone the following intensely *colored hydrocarbons* are formed:

$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!\!>C = C<\!\!\begin{array}{l} CH_3 \\ \\ CH_3 \end{array} \qquad \text{dimethylfulvene}$$

$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!\!>C = C<\!\!\begin{array}{l} CH_3 \\ \\ C_6H_5 \end{array} \qquad \text{methylphenylfulvene}$$

$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array}\!\!>C = C<\!\!\begin{array}{l} C_6H_5 \\ \\ C_6H_5 \end{array} \qquad \text{diphenylfulvene}$$

Courtot [75] has pointed out the similarity in chemical behavior of the CH_2 in cyclopentadiene with the corresponding group in fluorene and indene, which hydrocarbons are also colored. The fulvene derivatives, discovered by Thiele, polymerize on warming and absorb oxygen, by autoxidation much more rapidly than cyclopentadiene.[76] Stobbe and Dünnhaupt [77] have shown that cyclopentadiene polymerizes very slowly in the absence of oxygen and, unlike styrol, the polymerization is but very slightly affected by light.

4-Methyl-2-Ethylcyclopentadiene: When the ethyl ester of levu-

[73] Grignard & Courtot, *Compt. rend. 158,* 1763 (1914); Courtot, *Ann. chim. 4,* 5: (1915).
[74] *Ber. 33,* 666 (1900); *34,* 68 (1901).
[75] *Loc. cit.*
[76] Engler & Frankenstein, *Ber. 34,* 2933 (1901).
[77] *Ber. 52,* 1436 (1919).

linic acid in alcohol solution is condensed by sodium ethylate, an unsaturated cyclic dicarboxylic ester is formed which may have either of the two following structures,

$$\text{I.}\quad \begin{array}{lcccl} CH_3 - & C & - CH_2 - & C & - CO_2H \\ & \| & & \| & \\ & CH & \text{———} & C & - CH_2CH_2.CO_2H \end{array}$$

4-methylcyclopentadiene-1-carboxy-2-propionic acid

$$\text{II.}\quad \begin{array}{lcccl} CH_3 - & C & - CH_2 - & C & - CO_2R \\ & \| & & \| & \\ RO_2C - CH_2 - & C & \text{———} & C & - CH_3 \end{array}$$

2.4-dimethylcyclopentadiene-1-carboxy-3-acetic acid

The discoverers of the condensation of levulinic ester favor I as being the structure of the reaction product. The free acid melts at 218°, with evolution of carbon dioxide and formation of the hydrocarbon, the structure of which, if the above structure I proves to be correct, is 4-methyl-2-ethylcyclopentadiene. The hydrocarbon boils at 135°, but on distilling at ordinary pressure about one-third is polymerized, the tendency to polymerize evidently being abnormally great.[78]

Methylcyclopentane has been made synthetically by a number of methods and has been shown to be present in the light distillate from Russian petroleum. Methyl-cyclopentane-2-one is formed by heating the calcium salt of β-methyladipic acid. The ketone, boiling-point 143.5°, may be purified by the sodium bisulfite compound, then reduced to methylcyclopentanol-(2), boiling-point 150.5°–151°, and the latter reduced, by heating with concentrated hydriodic acid, to methylcyclopentane.[80] When made by reducing the iodide, 1-methyl-2-iodo-cyclopentane, by the copper zinc couple the hydrocarbon showed the following physical properties,[81] boiling-point 71°–72°, $d\,\frac{0°}{0°}$ 0.7664. It has an odor like well-refined gasoline. A mixture of concentrated sulfuric and nitric acid has little effect on it but fuming nitric acid alone reacts rather violently, acetic acid, carbon dioxide and water being the chief reaction products. Nitric acid Sp. Gr. 1.075, at 115°–120° gives chiefly the tertiary nitro derivative. According to Nametkin,[82] 2-nitro-1-methylcyclopentane is also formed, boiling-point 98°–99° at 40 mm., $d\,\frac{22°}{4°}$ 1.0381, and succinic and α-methylglutaric acids

[78] Duden & Freydag, *Ber.* *36*, 944 (1903).
[80] Konowalow, *J. Russ. Phys.-Chem. Soc.* *28*, 125.
[81] Markownikow, *Ber.* *30*, 1222 (1897).
[82] *J. Russ. Phys.-Chem. Soc.* *43*, 1603 (1911).

are also formed. The tertiary nitro derivative can be isolated from the secondary nitro derivatives by dissolving the latter in aqueous alkali. According to Markownikow [83] tertiary nitromethylcyclopentane boils at 92° (40 mm.) or at 177° at atmospheric pressure, with considerable decomposition. Both nitro derivatives give good yields of the corresponding amines when reduced by tin and hydrochloric acid. The tertiary amine may be converted into the corresponding tertiary alcohol by nitrous acid and after distilling, boiling-point 135°–136°, solidifies to crystals melting at 30°.

Chlorine reacts energetically with methylcyclopentane at ordinary temperatures in diffused daylight.[84] The tertiary chloride, prepared from the tertiary alcohol, is unstable, partially decomposing on distillation, boiling-point 123°. By direct chlorination of methylcyclopentane, derived from petroleum, Markownikow obtained a mixture of chlorides from which he was unable to isolate any definite product, the presence of cyclohexane in the original methylcyclopentane adding to the difficulty.

Methylcyclopentane has been made by means of the Grignard reaction, ring closing being brought about by treating δ-acetylbutyliodide with magnesium in ether,

$$\begin{array}{l} CH_2-CH_2-CO-CH_3 \\ | \\ CH_2-CH_2I \end{array} \xrightarrow{+\,Mg} \begin{array}{l} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{array} >C< \begin{array}{l} CH_3 \\ \\ OMgI \end{array}$$

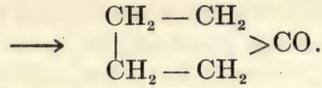
$$\begin{array}{l} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{array} >C< \begin{array}{l} CH_3 \\ \\ OH \end{array}$$

the alcohol being converted into the iodide and the latter reduced by zinc dust and acetic acid.[85]

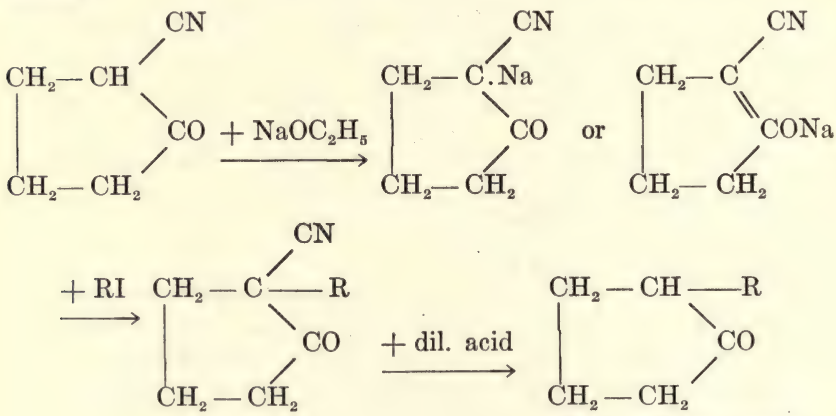
Cyclopentanone. This ketone has usually been prepared by ring closing of the ethyl ester of adipic acid by means of sodium. The resulting ester may be regarded as a carbocyclic derivative of acetoacetic ester and by the general method of decomposing such esters to ketones, this cyclic ester yields cyclopentanone,

$$\begin{array}{l} CH_2-CH_2-CO_2R \\ | \\ CH_2-CH_2-CO_2R \end{array} \xrightarrow{+\,Na} \begin{array}{l} CH_2-CH-\!\!-CO_2R \\ | \qquad\qquad\quad >CO \\ CH_2-CH_2 \end{array} \longrightarrow$$

[83] *Ann.* *307*, 355 (1899).
[84] Markownikow, *loc. cit.*
[85] Zelinsky & Moser, *Ber.* *35*, 2684 (1902).



Thorpe and Best [86] have described a series of derivatives of cyclopentanone which are quite stable to acids but are decomposed by alkali with rupture of the ring, the ring being stable to acids as long as a CN or $CO_2C_2H_5$ group is present adjacent to the ketone group. The corresponding imino derivatives are exceedingly stable to alkaline hydrolyzing agents. The derivative 2-cyanocyclopentane-1-one is a compound which resembles ethyl cyanoacetate in many of its properties; thus when treated with alcoholic sodium ethoxide it yields a sodium derivative which on treating with methyl iodide yields 2-cyano-2-methyl-cyclopentane-1-one. These derivatives will not be described in any detail but are mentioned since they show the great similarity in the chemistry of the open chain and cyclopentane series, and also since Best and Thorpe showed that the CN group could readily be removed by heating with dilute sulfuric acid yielding derivatives of cyclopentanone.



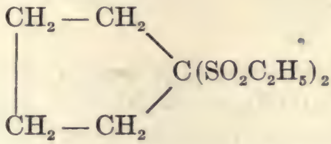
alkyl cyclopentanones.

Thorpe and Best also made 2.5-dimethylcyclopentane-1-one, boiling-point 149°, and 2-ethyl-cyclopentanone, boiling-point 149°, and 2-methylcyclopentanone by similar methods.

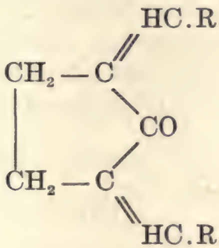
Cyclopentanone is formed during the carbonization of wood. It boils at 129°, d_{20° 0.948, n_D 1.4366.[87] Acetic anhydride enolizes it

[86] *J. Chem. Soc.* *95*, 690 (1909).
[87] Wallach, *Ann.* *353*, 330.

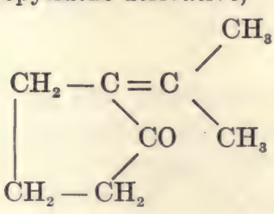
to form cyclopentenol acetate. The semicarbazone melts at 205°–207° when slowly heated, or at 212°–213° when heated rapidly. It condenses with formic acid ester to form oxymethylenecyclopentanone $C_5H_6O : CH(OH)$, melting-point 72°–73°. A cyclopentanonesulfonal is known melting at 127°–128°.



It condenses readily with aldehydes to form derivatives of the general type [88]

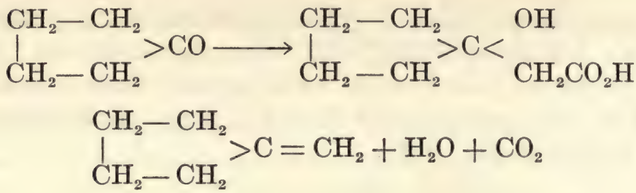


The condensation product of the above type formed with benzaldehyde melts at 191°, with anisaldehyde 215°, cinnamic aldehyde 222.5°, piperonal 257° and cuminol 145.5°. Acetone condenses with cyclopentanone [89] to form the isopropylidene derivative,

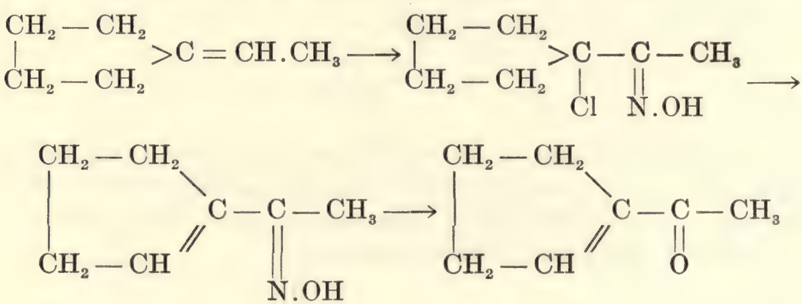


a liquid very soluble in water, boiling at 195°–199°. Another reaction which has been useful in the synthesis of hydrocarbons derived from cyclopentanone is the condensation with bromoacetic ester and zinc, according to Reformatsky's method, to give cyclopentanolacetic ester, the free oxy acid decomposing on heating to give *methenecyclopentane,*[90] boiling-point 78°–81°.

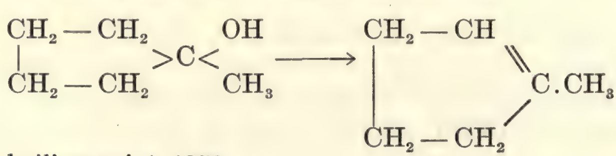
[88] Vorländer, *Ber.* *29*, 1838 (1896); Hobohm & Menzel, *Ber.* *36*, 1499 (1903); Wallach, *Goett. Nachr.* *1907*, 404.
[89] Wallach, *Ann.* *394*, 368.
[90] Wallach, *Ann.* *347*, 325.



Methenecyclopentane has a penetrating rather disagreeable odor, yields the glycol $C_6H_{10}(OH)_2$ on oxidation by permanganate and, following the general behavior of glycols, this glycol is converted by dilute acids to cyclopentane aldehyde. In the same manner α-bromopropionic acid yields the oxy acid from which *ethylidenecyclopentane* may be prepared. This hydrocarbon, boiling-point 114°, behaves like the terpenes in many of the characteristic reactions. Thus it yields a nitroso chloride, which on treating with alkali loses HCl and on hydrolyzing the resulting oxime, Δ^1-acetylcyclopentane, is formed,[91]

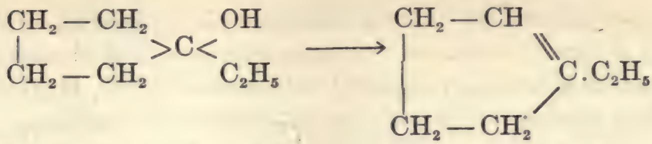


Cyclopentanone reacts normally with the Grignard reagent, giving 1-methylcyclopentanol(1) with methyl-magnesium iodide,[92] or the ethyl derivative with ethyl-magnesium iodide.[93] These tertiary alcohols readily decompose to give alkyl cyclopentenes



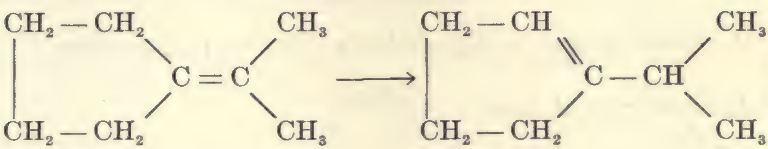
boiling-point 135°
melting-point 35°–37°

[91] Wallach, *Ann.* *365,* 274.
[92] Zelinsky & Namjetkin, *Ber.* *35,* 2683 (1902).
[93] Wallach, *Ann.* *365,* 276.



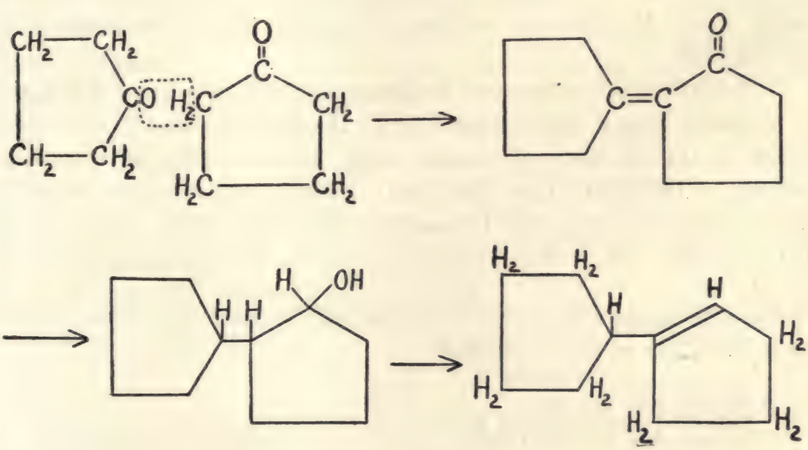
boiling-point 155°–157° $d_{21.5°}$ 0.916 — boiling-point 108° $d_{20°}$ 0.7915

By condensing with bromoisobutyric acid and decomposition of the resulting oxy acid, isopropylidenecyclopentane is formed, which, like terpinolene and other hydrocarbons having a semicyclic double bond of this nature, is converted to isopropylcyclopentene by alcoholic sulfuric acid, the double bond shifting to the ring,

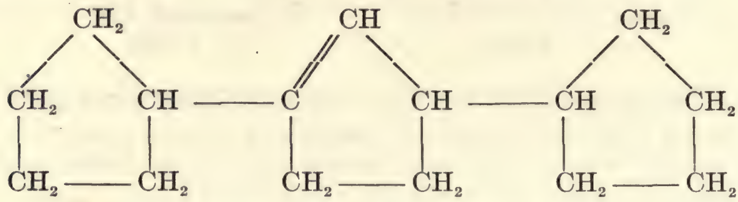


boiling-point 136°–137°
$d_{20°}$ 0.817

The reactivity of cyclopentanone is also shown by its condensation on treating with sodium ethylate or with hydrogen chloride to dicyclopentenepentanone, which may be reduced first by hydrogen and palladium and then by sodium to the saturated alcohol. Heating the alcohol with zinc chloride yields *cyclopentylcyclopentene,* boiling-point 197°–198°.



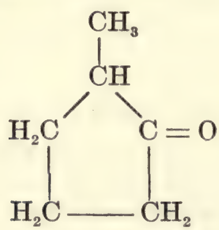
By the condensation of three molecules of cyclopentanone a ketone $C_{15}H_{20}O$ is formed, which on hydrogenation, as indicated above, yields the saturated ketone dicyclopentylcyclopentanone,[94] $C_{15}H_{20}O$, the corresponding alcohol readily yielding dicyclopentylcyclopentene,



boiling-point 290° at 760 mm., $d_{20°}$ 0.939

This hydrocarbon may be regarded as a tricyclic "sesquiterpene."

1.2-Methylcyclopentanone



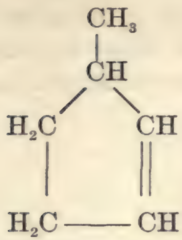
boiling-point 140°–141°

$d_{20°}$ 0.917

This ketone can be prepared from camphor-phorone, or from α-methyl adipic acid. It does not condense with aldehydes in the presence of caustic soda.

1.3-Methylcyclopentanone, boiling-point 144°–145°, $d_{22°}$ 0.913, can be prepared from β-methyladipic acid. It condenses readily with aldehydes in the presence of caustic soda, the benzaldehyde compound melting at 149°–151° (inactive form). When prepared from optically active β-methyladipic the 1.3-methylcyclopentanone is also active.[95] $[\alpha]_D$ + 124°–133°. When reduced to the alcohol and then converted to the iodide, the latter yields 1-methyl-Δ^2-cyclopentene when treated with alcoholic caustic potash.[96]

[94] Wallach, *Ann.* *389,* 182.
[95] Wallach, *Ann.* *332,* 349; *394,* 371.
[96] Zelinsky, *Ber.* *35,* 2488 (1902).

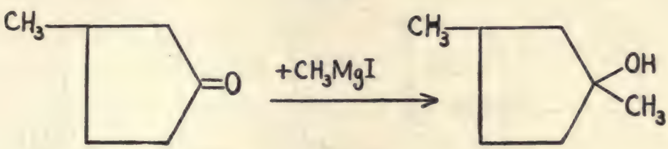


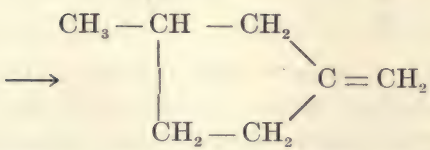
boiling-point 69°, $d\frac{18^\circ}{4^\circ}$ 0.7663

$[\alpha]_D + 59.07$

1-methyl-Δ^2-cyclopentene

1.3-Methylcyclopentanone reacts with methyl-magnesium iodide to give 1.3-dimethylcyclopentanol(3), boiling-point 143°–145°. According to Zelinsky this tertiary alcohol is decomposed by oxalic acid mainly to *1-methyl-3-methenecyclopentane,*[97]



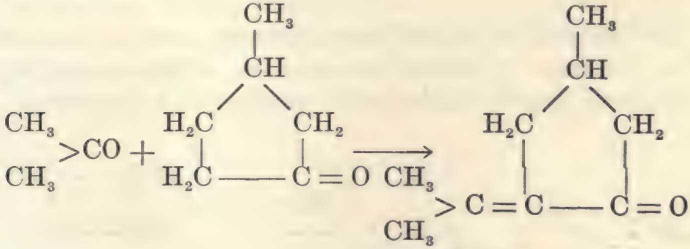


boiling-point 93°

$d\frac{19^\circ}{4^\circ}$ 0.7734

Potassium permanganate solution oxidizes 1-methyl-3-methene-cyclopentane to the glycol and 1.3-methylcyclopentanone.

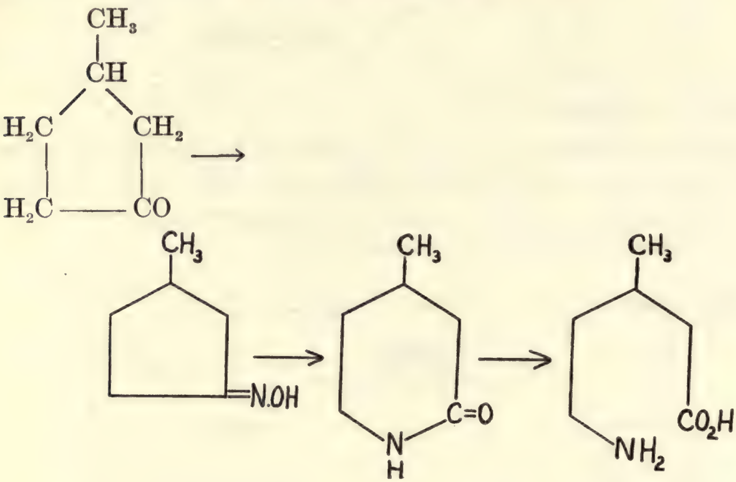
1.3-Methylcyclopentanone condenses with acetone [98] to form 4-isopropylidene-1-methylcyclopentane-3-one, which can be employed for the synthesis of a series of hydrocarbons containing the methyl and isopropyl groups in the 1.4 position.



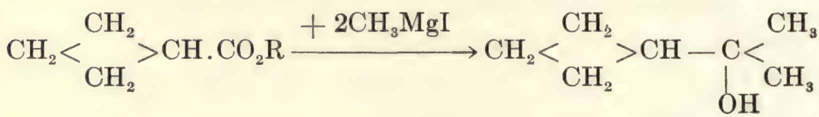
boiling-point 203°–205°
d — 0.9315

[97] *Ber.* *34*, 3950 (1901).
[98] Wallach, *Ann.* *394*, 372.

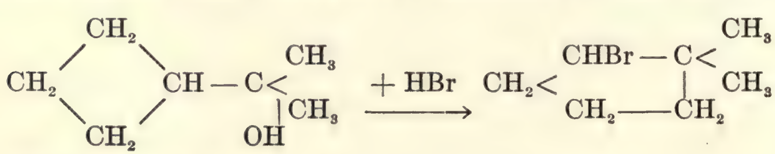
The ring may be broken by the rearrangement of the oxime, by sulfuric acid, to the isoxime and hydrolyzing the latter by boiling with hydrochloric acid to amidocapronic acid,[99] a reaction which is very generally applicable to the cyclic ketones.



1.1-Dimethylcyclopentane: Kishner[100] finds that all of the reactions of dimethylcyclobutylcarbinol, which were studied by him, are abnormal in that the cyclobutane ring is changed to the cyclopentane ring. The carbinol may be prepared by the Grignard reaction applied to the ester of cyclobutanecarboxylic acid,

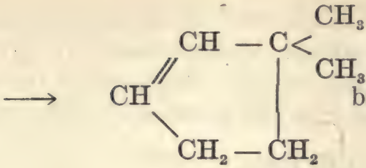


When this carbinol is treated with hydrogen bromide the product formed is 2-bromo-1.1-dimethylcyclopentane, which on treating with alcoholic caustic potash yields the Δ^2 unsaturated hydrocarbon.



[99] Wallach, *Ann.* *312*, 184

[100] *J. Russ. Phys.-Chem. Soc.* *40*, 994 (1908).



boiling-point 78°–78.5°

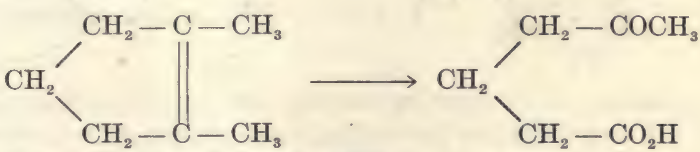
$d\frac{20°}{0°}$ 0.7580

$n\frac{20°}{D}$ 1.4190

It has an odor resembling naphthalene. On oxidation by nitric acid it yields αα-dimethylglutaric acid. According to Kishner,[101] both hydrobromic and hydriodic acids reacting on the above carbinol yield halogen derivatives, which on treating with alcoholic caustic potash yield 1.1.-dimethyl-Δ^2-cyclopentene together with the isomeric hydrocarbon 1.2-dimethyl-Δ^1-cyclopentene. When the bromide, obtained from the carbinol, is reduced by the copper-zinc couple, a saturated hydrocarbon is formed which Kishner[102] regards as *1.1 Dimethylcyclopentane,* boiling-point 88.3°–88.5°, $d\frac{20°}{0°}$ 0.7553.

1.2-Dimethylcyclopentane, obtained by reduction of 1.2-dimethyl-Δ^2-cyclopentene by Sabatier's method, boils at 92.7°–93°, $d\frac{20°}{0°}$ 0.7534, $n\frac{20°}{D}$ 1.4126.

1.2-Dimethyl-Δ^1-Cyclopentene, one of the products obtained by the decomposition of dimethylcyclobutylcarbinol, as described above, is identical with the hydrocarbon made by Maquenne[103] from perseitol. On reduction by means of concentrated hydriodic acid it is converted to a hydrocarbon C_7H_{17}, which Aschan[104] regarded as 1.3-dimethylcyclopentane, but Kishner[105] states that more probably it is 1.2-dimethylcyclopentane together with a little methylcyclohexane. The olefine reacts with hydrobromic acid to form an unstable bromide, yields a nitrosochloride melting at 73°–75°, and on oxidation yields γ-acetobutyric acid.



[101] *J. Russ. Phys.-Chem. Soc. 40,* 994 (1908).
[102] *J. Russ. Phys.-Chem. Soc. 37,* 509 (1905).
[103] *J. Chem. Soc. Abs. 1893* (1), 635.
[104] Chemie d. Alicyclischen Verb, p. 473.
[105] *J. Russ. Phys.-Chem. Soc. 40,* 994 (1908).

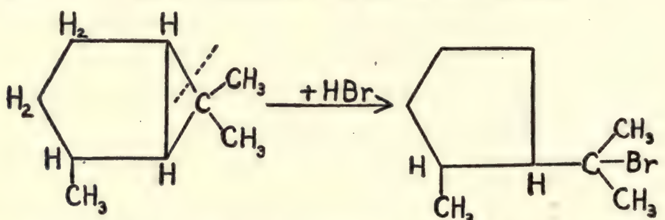
1.3-Dimethylcyclopentane was synthesized in an optically active form by Zelinksy[106] from *d.*-1.3-dimethylcyclopentanol(3) by converting the alcohol to the iodide and reducing the latter by the well-known method of treating with zinc dust and acetic acid. The hydrocarbon boils at 90.5°–91°, d $\frac{16^\circ}{4^\circ}$ 0.7497, $[\alpha]_D + 1.78^\circ$.

1-Methyl-3-Ethylcyclopentane was prepared in an optically active form by Zelinsky in a manner similar to that employed for the 1.3-dimethyl derivative. The hydrocarbon boils at 120.5°–121°, d $\frac{16^\circ}{4^\circ}$ 0.7669, $[\alpha]_D + 4.34^\circ$. It is noteworthy that the optical rotations of the active saturated hydrocarbons are usually much lower than the unsaturated hydrocarbons of the same carbon atom structure.

1-Methyl-3-Isopropylcyclopentane[107] is formed by reducing camphorone by Sabatier's method at 130° to dihydrocamphorone, which on further reduction yields the saturated hydrocarbon, boiling-point 132°–134°, d_{19° 0.773.

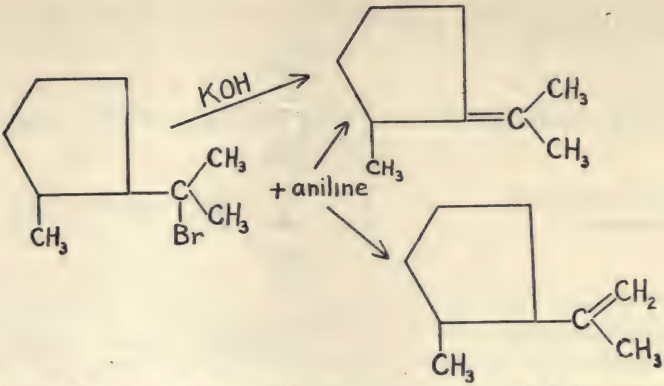
1.2-Dimethyl-3-Isopropylcyclopentane[107] has also been made from camphorone by hydrogenation to dihydrocamphorone and treating this ketone with methyl-magnesium iodide, decomposing the resulting tertiary alcohol and hydrogenating the resulting cyclopentene derivative. The saturated hydrocarbon boils at 146°–148°, d_{16° 0.786.

1-Methyl-2-Isopropylcyclopentane: When the bicyclohexane derivative prepared by Kishner from camphorone by his hydrazine method, is treated with hydrogen bromide the three-carbon ring is broken in such a way as to form a *cyclopentane* derivative, a very general result when it is theoretically possible to form either a cyclopentane or cyclohexane derivative by the rupture of a three-carbon ring.



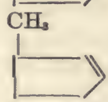
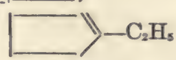
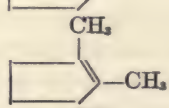
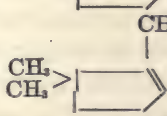
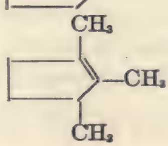
Decomposition of the resulting bromide with alcoholic caustic potash yields the isopropylidene derivative almost exclusively but decomposition by aniline gives the two possible isomers.

[106] *Ber.* *35*, 2677 (1902).
[107] Godchot & Taboury, *Compt. rend.* *156*, 470; *Bull. soc. chim.* (4) *13*, 599 (1913); *Compt. rend.* *172*, 686 (1921).



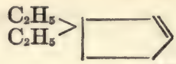
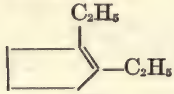
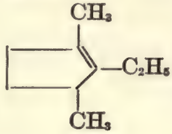
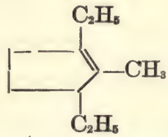
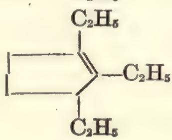
Both of the above unsaturated hydrocarbons on catalytic hydrogenation yield 1-methyl-2-isopropylcyclopentane, boiling-point 142.5°, d $\frac{15°}{0°}$ 0.7833.

CYCLOPENTENES. PHYSICAL PROPERTIES *

Name	*Formula*	*B.-P °C*	$d\frac{20°}{4°}$	$n\frac{20°}{4°}$
Cyclopentene		44.5°	0.773	1.421
Methyl-Δ²-cyclopentene		69. °	0.765	1.413
Methyl-Δ³-cyclopentene		72. °	0.772	1.427
Ethyl cyclopentene		108. °	0.796	1.443
1.1-dimethyl-Δ²-cyclopentene		78. °	0.758	1.419
1.2-dimethyl-Δ¹-cyclopentene		103. °	0.794	1.442
1.1.2-trimethyl-Δ²-cyclopentene		108. °	0.782	1.431*
1.2.3-trimethyl-Δ¹-cyclopentene		119. °	0.796	1.442*

* Auwers, *Ann.* *415*, 110 (1918).

** The refractive indices marked with an asterisk are for $n\frac{20°}{\alpha}$.

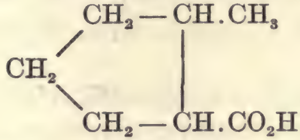
1.1-diethyl-Δ^2-cyclopentene		144. °	0.808	1.446
1.2-diethyl-Δ^1-cyclopentene		151.5°	0.812	1.452
1.3-dimethyl-2-ethyl-Δ^1-cyclopentene		140. °	0.803	1.447*
1.3-diethyl-2-methyl-Δ^1-cyclopentene		164. °	0.811	1.450*
1.2.3-triethyl-Δ^1-cyclopentene		181.5°	0.814	1.451*

Naphthenic Acids: These acids probably occur in more petroleums than is commonly supposed, although they are usually associated with Russian petroleum. The naphthenic acids occurring in Russian petroleum include relatively simple low-boiling acids so that the mixture of acids, as they are obtained by treating with aqueous alkali and precipitating with acid, possesses a marked, very persistent and rather disagreeable odor. The Gulf Coast petroleums also contain organic acids but they are of high boiling-point and, when separated from lubricating oil, are practically odorless and are easily salted out of their solutions in aqueous solutions. The acids in the Gulf Coast oils have never been studied to the extent of determining their nature, but their alkali solutions have pronounced emulsifying and foam producing power and may accordingly find employment in compounding cutting oils or emulsions but can hardly be employed in soaps on account of the ease with which their alkali salts, or soaps, are salted out.

Markownikow [108] fractioned the methyl esters of the Russian naphthenic acids. The fraction distilling at 160°–165° was essentially $C_7H_{11}O_2CH_3$. The purified free acid distilled at 213°–214° and the purified methyl ester boiled at 164°–166°, d $\frac{20°}{0°}$ 0.90509. The amide

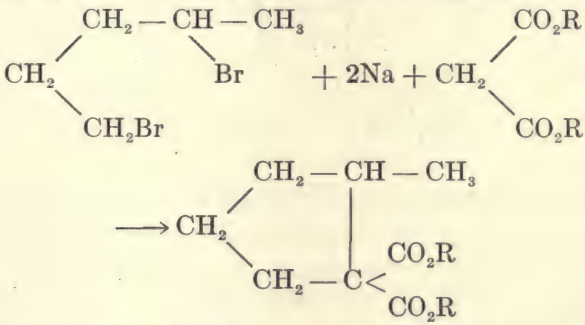
[108] *Ann.* **307**, 369 (1899).

melts at 121°–123.5° and by converting the amide to the amine, a secondary amine was formed which is perhaps identical with the secondary amine resulting from the reduction of secondary nitromethylcyclopentane. The acid methylcyclopentane-2-carboxylic acid



isolated by Perkin and Freer,[109] boils at 219°–219.5° and an isomeric acid, probably the 1.3 acid, prepared by Euler,[110] boils at 220°. The aldehyde derivatives of methylcyclopentane have been observed by Markownikow and the two synthetic acids has not been satisfactorily explained.

The starting point in the researches of Perkin and Freer [111] was the condensation of sodio-malonic ester with 1.4-dibromopentane,



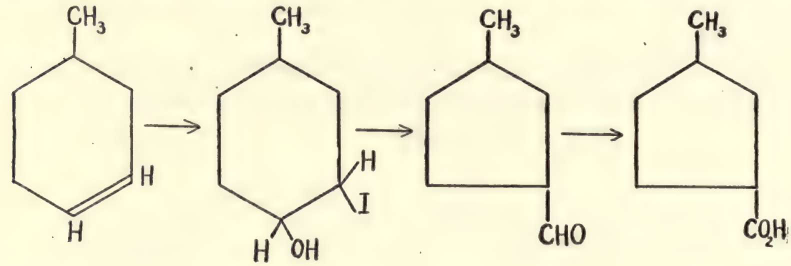
On heating the free dicarboxylic acid a few degrees above its melting-point it decomposes to carbon dioxide and *1-methylcyclopentane-2-carboxylic acid,* boiling-point 219.5°–220.5°. These carboxylic acid derivatives of cyclopentane are of interest since the simpler naphthenic acids of Russian petroleum are evidently derivatives of cyclopentane. The acid named above has a most disagreeable odor, somewhat resembling valeric acid. It is not acted upon by bromine at ordinary temperatures but at 100° rapid substitution occurs with evolution of hydrogen bromide.

Zelinsky[112] has applied the Grignard reaction to the preparation of naphthenic acids but the yields are usually very poor. From 1-methyl-

[109] *J. Chem. Soc.* *53,* 199 (1888).
[110] *Ber.* *28,* 2952.
[111] *J. Chem. Soc.* *53,* 195 (1888).
[112] *Ber.* *35,* 2687 (1902).

3-bromo-cyclopentane the acid *1-methylcyclopentane-3-carboxylic acid* was prepared by passing carbon dioxide into the ethereal solution of the magnesium derivative. The acid distills at 115°–116° (15 mm.), $d\,\frac{22^\circ}{4^\circ}$ 1.006; the amide melts at 149°–150°. This acid is possibly identical with the methylcyclopentanecarboxylic acid described by Euler, referred to above.

Rearrangements of the iodohydrins of the methylcyclohexenes to aldehyde derivatives of methylcyclopentane have been observed by Tiffeneau.[113] Thus the iodohydrin of Δ^3-methylcyclohexene, on treating with silver nitrate is converted into the aldehyde, which on oxidation yields the corresponding acid, previously obtained by Zelinsky,



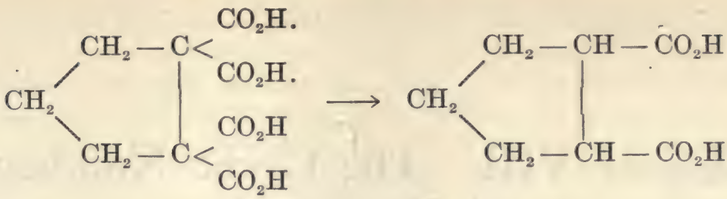
The iodohydrin of cyclopentene does not rearrange but gives the 1.2-oxide. In the case of the phenylcyclohexane derivative[114] or substituted phenyl derivatives, rearrangement to the cyclopentane ring does not take place but the phenyl group migrates to the α-position with the formation of a cyclohexenol, which is converted to the isomeric ketone.

Cyclopentane-1.2-Dicarboxylic Acid has been prepared from 1.3-dibromopropane and sodium-malonic ester and also by the action of iodine on the disodium derivative of the ester,

$$CH_2\begin{cases} CH_2-C.Na(CO_2R)_2 \\ \\ CH_2-C.Na(CO_2R)_2 \end{cases} + I_2 \longrightarrow CH_2\begin{cases} CH_2-C(CO_2R)_2 \\ \quad\quad\quad\;\; | \\ CH_2-C(CO_2R)_2 \end{cases}$$

and decomposing the tetracarboxylic acid by heating, in the usual manner,

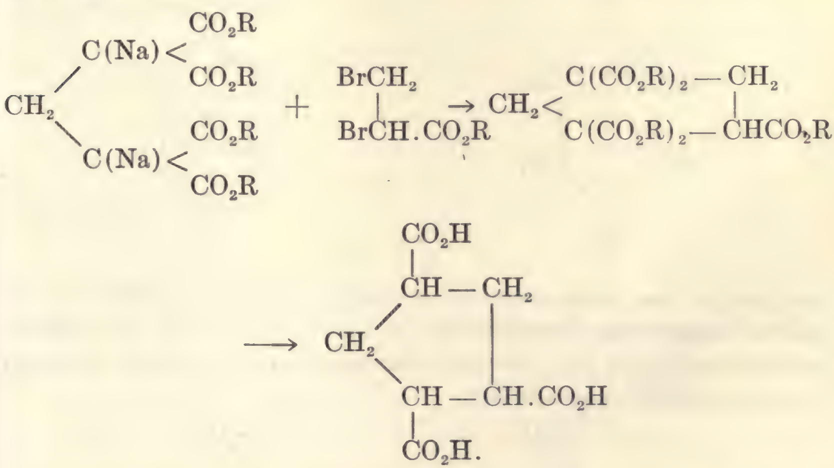
[113] *Compt. rend.* *159*, 771 (1914).
[114] Le Brazidec, *Compt. rend.* *159*, 774 (1914).



It is known in *cis* and *trans* forms, the *cis* form readily forming an anhydride.

1-Methylcyclopentane-2.3-Dicarboxylic Acid, melting-point 99°–104°, has also been prepared by one of Perkin's methods, i. e., condensing 1.3-dibromobutane with the disodium derivative of the ethyl ester of ethane tetracarboxylic acid, followed by decomposition of the tetracarboxylic acid in the usual manner.[115]

The *cis* and *trans* modifications of cyclopentane 1.2.4-tricarboxylic acid are known, and are best prepared by the reaction of ethyl αβ-dibromo-propionate on the disodium derivative of ethyl propane-α α γ γ-tetracarboxylate.[116]



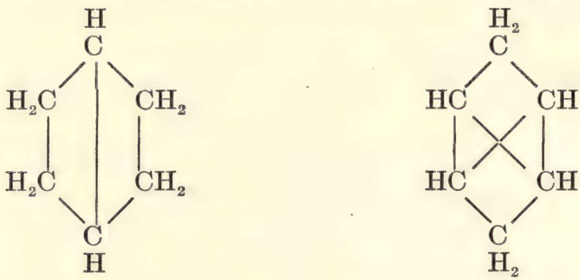
The *trans* form, melting-point 129°–130°, yields the anhydride of the *cis* form when heated with acetic anhydride and the anhydride then may be hydrolyzed to the pure *cis* form, melting at 146°–148°.

[115] Fargher, *J. Chem. Soc. 117,* 1355 (1920).
[116] Perkin & Goldsworthy, *J. Chem. Soc. 105,* 2666 (1914).

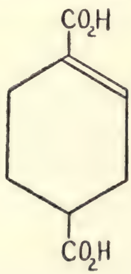
Chapter VIII. The Cyclic Non-benzenoid Hydrocarbons.

The Cyclohexane Series.

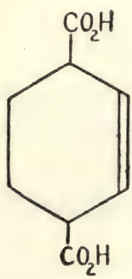
The conception of cyclohexane and its derivatives as "hydroaromatic" compounds has served a useful purpose in connection with the study of the constitution of benzene. Reduction of ortho, meta and para derivatives of benzene yield the corresponding derivatives of cyclohexane which would not be expected from Ladenburg's prism formula. It has also been shown that tetrahydrobenzene and dihydrobenzene do not have the bridged structures shown below,



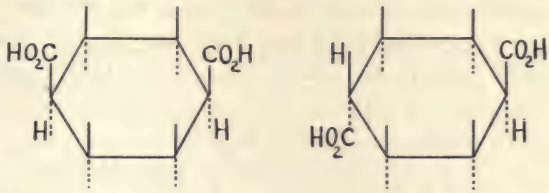
and Baeyer has shown that the tetrahydroterephthalic acids do not possess bridged ring structures but contain double bonds, the addition products indicating that the two isomeric acids have double bonds in the two positions shown below,



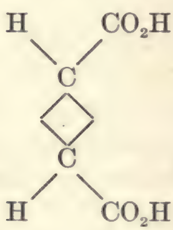
and



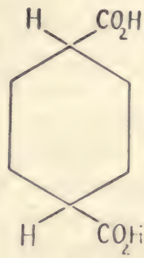
It should be borne in mind that derivatives of hydrocarbons such as cyclohexane are capable of exhibiting stereoisomerism when two or more substituents are present. Thus if the six carbon atoms are conceived to lie in one plane, as in the plane of the paper, then six of the hydrogen atoms in cyclohexane will lie above the plane and six below the plane. Cyclohexanecarboxylic acid can obviously exist in only one form but a cyclohexane dicarboxylic acid can exist in two forms. Thus the 1.4-dicarboxylic acid derived from terephthalic acid, studied by Baeyer, can exist in two stereo isomeric forms,



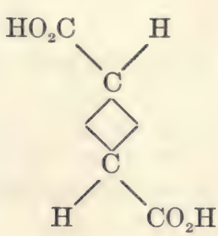
Baeyer likened these stereoisomers to fumaric and maleïc acids, considering the double bond and the ring structure as preventing free rotation in much the same manner,



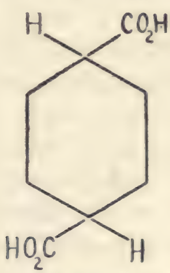
maleïc acid



maleinoid cyclohexane-1.4-dicarboxylic acid



fumaric acid



fumdroid cyclohexane-1.4-dicarboxylic acid

Cyclohexane and its alkyl derivatives probably occur in more petroleums than is generally known but this hydrocarbon and its monomethyl and dimethyl derivatives were long ago recognized as important constituents of the light naphtha from Russian petroleum, hence the term "naphthenes" suggested by Markownikow. Careful examination of the lighter distillates of the petroleums from southern California, Mexico and the southern Texas and Louisiana fields will undoubtedly show the presence of cyclohexane and its simpler alkyl derivatives. Quite a variety of methods have been employed for the preparation of cyclohexane and its derivatives but the methods of catalytic hydrogenation of Sabatier and Senderens Ipatiev and Skita are so far superior to most of the others that the latter are generally only of historical interest. A number of syntheses of cyclohexane and its derivative will be briefly mentioned, as follows:

(1) Treatment of 1.6-dibromohexane with sodium.[1]

(2) Reaction of 1.5-dibromopentane, malonic ester and sodium ethylate, yielding cyclohexane-1.1-dicarboxylic acid, which in turn yields cyclohexanecarboxylic acid by decomposition.

(3) Heating the calcium salt of pentane-1.5-dicarboxylic acid, forming cyclohexanone.[2]

(4) Condensation of the ethyl ester of pentane-1.5-dicarboxylic acid to form the ester of cyclohexanone-2-carboxylic acid.

(5) Condensation of two molecules of succinic ester[3] to the 2.5-dicarboxylic acid derivative of the 1.4-cyclohexane-dione; this readily loses CO_2 to give the 1.4-diketone, which can be reduced by the usual methods to 1.4-cyclohexanediol from which cyclohexane may be prepared by reducing with hydriodic acid or the iodide converted into $\Delta^{1.4}$-cyclohexadiene.

(6) Condensation of δ-ketonic acids to 1.3-cyclohexanediones.

(7) Addition of sodium malonic ester to α β unsaturated ketones to form derivatives of 1.3-cyclohexanedione.

(8) Condensation of two molecules of acetoacetic ester with aldehydes to form open chain diketonic acids which condense further to cyclic unsaturated ketonic esters which readily lose CO_2 on saponification to give cyclohexenone derivatives. Similar products are obtained by the condensation of methylene iodide and two molecules of sodium acetoacetic ester.[4]

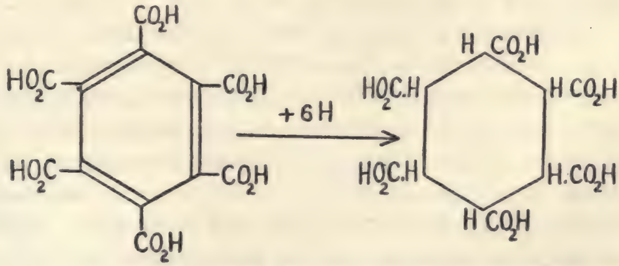
[1] W. H. Perkin, Jr., *Ber.* *27*, 216 (1894).
[2] Markownikow, *Compt. rend.* *110*, 466 (1890); *115*, 462 (1892).
[3] Baeyer, *Ann.* *245*, 106 (1888); *Ber.* *23*, 1276 (1890).
[4] Hagemann, *Ber.* *26*, 876 (1893).

(9) Condensation of aliphatic aldehydes and ketones, for example, methyl heptenone to a mixture of meta-xylene and dimethylcyclohexene; citronellal to isopulegol, etc.

(10) Addition of chlorine to benzenoid hydrocarbons, for example, the addition of chlorine to benzene to form hexachlorocyclohexane.

(11) The indirect reduction of unsaturated substances by first adding bromine or hydrobromic acid and then replacing the bromine by hydrogen by treating with acetic acid and zinc, for example the conversion of dihydro and tetrahydroterephthalic acids to cyclohexane-1.4-dicarboxylic acid.

(12) The hydrogenation or reduction of benzenoid hydrocarbons. As mentioned above, these methods, particularly the well-known method of Sabatier and Senderens, have practically superseded all the older methods and promise to become of industrial importance for the hydrogenation of benzene to cyclohexane, phenol to cyclohexanol and cyclohexanone, both the latter products being of value as commercial solvents (see below). The ease of reduction or hydrogenation varies considerably with the number and character of the substituent groups. Thus terephthalic acid and the dihydro and tetrahydro-terephthalic acids are reduced with difficulty, but mellitic acid is easily reduced by reducing agents to cyclohexanehexacarboxylic acid.



With the phenols the ease of reduction increases with the number of hydroxyl groups, resorcin being easily reduced to cyclohexane-1.3-dione.

Benzene is reduced to cyclohexane in the presence of catalytic nickel at 180°–250°, but the refinements of the process as carried out industrially are not generally known. Cyclohexane was manufactured in this way in the United States and in Germany during the recent war, the cyclohexane being used to some extent as a motor fuel [5] for aeroplanes. In the case of the alkyl derivatives of benzene some decompo-

[5] Dayton Metal Products Co. Brit. Pat. 133,288; 133,667 (1919).

sition also takes place, for example, in the hydrogenation of para-cymene at 170°–180° to para-menthane, small proportions of methyl and ethylcyclohexane are also formed. At about 300° the mixture in equilibrium in the presence of nickel consists chiefly of benzene and at this temperature dehydrogenation of cyclohexane to benzene can be effected. The relative ease with which this change is brought about makes possible the detection of small proportions of cyclohexane in the presence of normal hexane, and other saturated hydrocarbons, the fraction distilling at 75°–85° being passed over nickel at 300° and the distillate treated with concentrated sulfuric acid to remove and polymerize olefines and then treated with nitrating acid mixture to remove the benzene which may be identified as crystalline dinitrobenzene.[6] As regards the hydrogenation of benzene to cyclohexane by hydrogen in the presence of platinum black Willstätter and Hatt[7] show that the reaction proceeds quantitatively at atmospheric pressures in about six hours in glacial acetic acid solution, using about 0.1 part of platinum black. The hydrogenation is distinctly slower when glacial acetic acid is not used as a solvent. The catalyst is exceedingly sensitive to traces of thiophene, less than 0.01 mg. of thiophene per gram of benzene completely preventing the hydrogenation. Toluene is reduced to methylcyclohexane under the same conditions much more readily than in the case of benzene, i. e., in about 3½ hours.

The hydrogenation of benzene derivatives to the corresponding derivatives of cyclohexane may conveniently be considered here. Aschan[8] reduced sodium benzoate by sodium amalgam, neutralizing the caustic soda by carbon dioxide, as fast as formed, thus preventing the precipitation of the sodium benzoate by the concentrated caustic soda. When the hydrogenation is incomplete a considerable proportion of Δ^2-cyclohexene carboxylic acid is formed. Ipatiev[9] obtained yields of 40 to 50 per cent of cyclohexane carboxylic acid by his method of reducing at 300°–320° and hydrogen at about 210 atmospheres in the presence of nickel oxide. Phthalic acid under the same conditions is more readily reduced to the corresponding cyclohexane-1.2-dicarboxylic acid and this method is probably the best method of

[6] Tausz, *Chem. Ztg.* *37*, 334 (1914). According to Zelinsky (Cf. Wieland, *Ber.* *45*, 484 [1912]), hydrogen is dissociated from cyclohexane, with the formation of benzene, at temperatures below 300° and in the presence of nickel; under the same conditions cyclopentane and cycloheptane are stated to be practically unchanged. In the absence of a catalyst cyclohexane yields considerable benzene at 490°; normal hexane at slightly higher temperatures yields methane, amylene and other hydrocarbons. (Jones, *J. Chem. Soc.* *107*, 1582 [1915].)

[7] *Ber.* *45*, 1471 (1912).

[8] *Ber.* *24*, 1864 (1891).

[9] *Ber.* *41*, 1005 (1908).

preparing this acid. It is noteworthy that at the same temperatures and with the same catalyst but without the use of pressure no hydrogenation of phthalic acid could be detected. The older method of reduction by means of sodium and amyl alcohol was used successfully for the reduction of anthranilic acid to 2-amidocyclohexanecarboxylic acid, and also para-amidobenzoic acid to 4-amidocyclohexanecarboxylic acid.[10] Osterberg and Kendall[11] used sodium and alcohol for the reduction of the oxime of cyclohexanone to cyclohexylamine and also report that the method of Sabatier and Senderens gives good yields of the amine from the oxime, but state that the method of reducing aniline to cyclohexylamine, according to Ipatiev, did not give satisfactory results. Ipatiev reported yields of 40 to 50 per cent of the amine by reducing aniline with hydrogen and nickel oxide, employing a hydrogen pressure of about 120 atmospheres at 220°–230°. Quinoline could not be hydrogenated by Padoa and Carughi,[12] using the method of Sabatier and Senderens, but Ipatiev succeeded in reducing it to decahydroquinoline by his high pressure method. Diphenylamine also cannot be reduced to dicyclohexylamine by the Sabatier and Senderens method, other products being formed, but the Ipatiev method, at 225°–230°, gives a good yield of dicyclohexylamine.[13] Paals' method on aniline is reported to give a yield of about 10 per cent of cyclohexylamine. Osterberg and Kendall recommend Ipatiev's method for the preparation of cyclohexane and cyclohexanol. Ipatiev finds that nickel oxide hydrogenates benzene and its derivatives several times faster than reduced nickel in the presence of hydrogen under pressure at about 255°. The cyclohexane so produced is practically pure and the reduction is complete in about 1½ hours when using 2 g. nickel oxide to 25 g. benzene. Decomposition with the formation of methane and the separation of carbon begins to be noticeable at about 290°. Under the same conditions Ipatiev reduced phenol to cyclohexanol, diphenyl to dicyclohexyl, naphthalene (in two successive operations) to decahydronaphthalene, dibenzyl to dicyclohexylethane, β-naphthol to β-hydroxydecahydronaphthalene and α-naphthol to α-hydroxydecahydronaphthalene. Anthracene was reduced by Godchot[14] by reduced

[10] Einhorn & Meyenburg, *Ber.* 27, 2466 (1894). In the case of anthranilic acid the reaction proceeds in two ways, pimelic acid also being formed, probably through the intermediate formation of salicylic acid.

$$C_6H_4<\begin{matrix}NH_2\\CO_2H\end{matrix} \longrightarrow C_6H_4<\begin{matrix}OH\\CO_2H\end{matrix} + H_2O + 4H \longrightarrow \begin{matrix}CH_2CH_2CO_2H\\|\\CH_2CH_2CH_2CO_2H\end{matrix}$$

[11] *J. Am. Chem. Soc.* 42, 2616 (1920).
[12] *Atti. Accad. Lincei* (5) 15, 113 (1907).
[13] Ipatiev, *Ber.* 41, 991 (1908); 40, 1281 (1907).
[14] *Compt. rend.* 139, 605 (1904).

nickel at atmospheric pressure to tetra and octohydroanthracene, but Ipatiev succeeded in completely reducing it to perhydroanthracene, $C_{14}H_{24}$, by his high pressure method, using nickel oxide as a catalyst. By one operation tetrahydroanthracene, melting-point 103°–105°, is the chief product; a second operation yields mainly decahydroanthracene, $C_{14}H_{20}$, melting-point 73°–74°, and a third operation using the decahydroanthracene yields the completely reduced hydrocarbon, $C_{14}H_{24}$, melting-point 88°–89°. Slight carbonization and formation of methane occurs at the temperatures employed, i. e., 260°–270°. Phenanthrene was also reduced in steps, the completely reduced hydrocarbon being finally obtained. At lower temperatures the hydrocarbon was not completely reduced, the temperatures required being considerably higher than for the reduction of benzene,

At 320° phenanthrene $\longrightarrow$ chiefly $C_{14}H_{12}$ and $C_{14}H_{14}$
At 360° " $\longrightarrow$ " $C_{14}H_{18}$
At 370° " $\longrightarrow$ " $C_{14}H_{24}$

The completely reduced phenanthrene is a liquid boiling at 270°–276°, does not crystallize at — 15° and is inert in the cold to nitrating acid mixture, bromine and aqueous permanganate. Phenyl ether is decomposed under the conditions of Ipatiev's method, yielding a mixture consisting of cyclohexane, cyclohexanol and cyclohexyl ether (temperature employed 230°).

As regards the practicability of developing Ipatiev's method into an industrial process, it may be pointed out that the pressures employed are at least no higher than the lowest pressures employed for the synthesis of ammonia from nitrogen and hydrogen, and the temperatures required are very much lower. The technique of operating at such pressures on an industrial scale has been improved to a degree which should make Ipatiev's process entirely feasible industrially. In connection with the hydrogenation of complex benzenoid hydrocarbons it should be noted that attempts have recently been made to hydrogenate coal under high pressures to oily hydrocarbon mixtures from which oily hydrocarbons, or polynaphthenes having lubricating value, may be obtained. This work, the details of which are not yet available, are undoubtedly based upon the earlier findings of Bergius [15] that, under

[15] According to U. S. Pat. 1,342,790, issued to F. Bergius, pulverized coal is mixed with a mineral oil boiling above 200° and introduced as a thick paste into a reaction vessel, where it is heated to about 400° and subjected to the action of hydrogen, without introducing any catalytic substance, under a pressure of 100 atmospheres. Partial hydrogenation is claimed, a heavy oil boiling about 300°-400° being formed from the coal substance. Bergius claims that with soft coals as much 85% of the coal may thus be converted into oily liquid or oil soluble products.

very high pressures, hydrogenation can be effected without a catalyst. For the hydrogenation of such an impure material as coal, it is obvious that either a high pressure method of the Bergius type, or the employment of a catalyst not poised by sulfur, will be required.

Skita has shown that the benzene ring may be reduced at ordinary temperatures by colloidal platinum. Thus cinnamic aldehyde is converted into cyclohexyl propyl alcohol by reduction in this way using very slight pressures, i. e., about one atmosphere. Cyclohexanone is also very rapidly reduced to cyclohexanol in the same manner. Acetic acid is usually employed as a solvent. The unsaturated ketone pulegone also yields the saturated alcohol menthol under the same conditions.[16] For research and laboratory preparations, Skita's method is usually to be preferred although the method does not appear to have been applied to many reductions of the benzene nucleus. Aqueous alcohol may also be employed as a solvent. In the reduction of pulegone to menthol 5 grams, in 40 c.c. acetic acid, and with colloidal platinum and a little gum arabic as a protective colloid to retard precipitation of the metal, the reduction is complete in sixty minutes.

Cyclohexane: The presence of cyclohexane in Russian petroleum was shown by Markownikow[17] and Young found it also in a specimen of gasoline from an American petroleum, but the exact origin of the oil examined by Young is not known. Its presence in the fraction boiling at 80°–81° may be indicated by the physical constants of the fraction and the isolation of adipic acid among the products of oxidation by nitric acid. The boiling-point is usually given as 80.8°, but the physical properties of a specimen of the hydrocarbon carefully purified by several treatments with slightly fuming sulfuric acid are given by Auwers[18] as follows, boiling-point 80.0°–80.2° at 749 mm., $d\ \frac{11.2^\circ}{4^\circ}$ 0.7869, n_D 1.42910, M_D 27.66 (calculated 27.71).

Cyclohexane is slightly more stable to heat than normal hexane, but the decomposition of both is noticeable at 500° and under pressure. According to Ipatiev[19] it is decomposed at 500°–510° and in the presence of alumina (110 atmospheres pressure) to a complex mixture of decomposition products among which methyl cyclopentane was identified by means of the easily formed tertiary nitro derivative

[16] *Ber.* *48*, 1496 (1915).
[17] *Ber.* *30*, 974 (1897).
[18] *Ann.* *410*, 262 (1915).
[19] *J. Russ. Phys.-Chem. Soc.* *43*, 1431 (1912).

$$\begin{array}{l} CH_2-CH_2 \\ | \qquad\qquad\quad >C< \\ CH_2-CH_2 \end{array} \begin{array}{l} NO_2 \\ \\ CH_3 \end{array}$$

Cyclohexane is practically inert to bromine in the cold and is only very slowly reacted upon at its boiling-point and in diffused daylight, but bromination is rapid in direct sunlight. In the presence of anhydrous aluminum bromide a mixture of high boiling products is formed, but when dibromo cyclohexane or cyclohexene is similarly treated it is possible to identify hexabromobenzene among the reaction products.[20]

Considerable has been written about the so-called *"formolite" reaction* which, according to Nastjukow, the cyclohexenes and other non-benzenoid cyclic hydrocarbons undergo when treated with formaldehyde in the presence of concentrated sulfuric acid or aluminum chloride. According to Nastjukow [21] a mixture of cyclohexane, anhydrous aluminum chlorine and trioxymethylenes react forming a mixture of condensation products but no definite reaction product was isolated. The reaction is usually carried out using sulfuric acid as the condensing reagent and the saturated acyclic hydrocarbons are supposed not to give the "formolite" reaction. It does not appear that any definite reaction products have ever been isolated and the character of the reaction therefore is at present a matter of speculation; also it does not appear that the reaction has been carried out with a sufficient number of pure hydrocarbons to warrant the proposal that it be employed in the study of petroleum fractions to determine what types of hydrocarbons are present. As carried out according to Nastjukow one volume of the hydrocarbon mixture is treated with one volume of concentrated sulfuric acid and then one-half volume of concentrated (40%) formaldehyde is gradually added, with agitation. A precipitate is formed which after washing with gasoline, water and ammonia, may be dried and powdered, the product resembling a brown resin. The higher boiling oils generally yield larger proportions of "formolite" resin than the lighter oils, but the yield of resin appears to vary evidently with the conditions of the operation. The product prepared according to Nastjukow's directions contains considerable sulfur, a spindle oil giving a resin containing 6.98 per cent sulfur and 6.66 per cent oxygen. When the mixture is kept cold the condensation product is liquid and does not contain sulfur.[22] According to Gurwitsch [23] only

[20] Bodroux & Taboury, *Bull. soc. chim. 9*, 592 (1911).
[21] *J. Russ. Phys.-Chem. Soc. 47*, 46 (1915).
[22] *J. Russ. Phys.-Chem. Soc. 42*, 1596 (1910).
[23] Wissensch, Grundlagen d. Erdölbearb., 46.

certain olefines such as "partially reduced aromatic compounds" and aromatic hydrocarbons react to give formolite resins. Terpenes are said to give "formolite" resins, but they are very energetically polymerized, oxidized and esterified by sulfuric acid alone and it is entirely obscure what the function of the formaldehyde is supposed to be. Most books on petroleum testing describe the "formolite" reaction and often use the phrase "formolite number," but this test and these phrases are meaningless until the reaction is studied in many cases, not only of cyclohexane, the cyclohexenes, and commercial oils of known chemical character, but also applied to a series of definite pure hydrocarbons of various types. Cyclohexenes should give "formolite" resins since they polymerize readily with sulfuric acid alone and cyclohexadiene reacts violently with sulfuric acid. Nastjukow may have discovered something, but, if so, no one has been able to determine what it is.

A series of metallo derivatives of cyclohexane has been prepared by Grüttner,[24] who has prepared cyclohexyl derivatives of lead, tin and bismuth. The starting point in all cases was the reaction of cyclohexyl magnesium bromide on the chloride or bromide of the other metal. Bromocyclohexane reacts with magnesium in ether very much like n.hexyl bromide, the secondary reaction

$$RMgBr + R.Br \longrightarrow MgBr_2 + R.R.,$$

taking place in both cases. The cyclohexyl derivatives show slight differences from the simple alkyl derivatives of lead. Tetracyclohexyl lead reacts with hydrogen chloride or hydrogen bromide to give

$$Pb\begin{matrix}/\!\!/ X_2 \\ \backslash\!\!\backslash (C_6H_{11})_2\end{matrix}$$

and the simple alkyl derivatives give $Pb\,X.R_3$ under the same conditions. Cyclohexyl-magnesium bromide and lead chloride in ether react very smoothly. Tetracyclohexyl tin crystallizes in fine microscopic aggregate melting at 248° and is easily soluble in benzene, chloroform and carbon bisulfide; bromine reacts with it to give $SnBr_2(C_6H_{11})_2$, long well formed needles melting at 58°. Tiffeneau and Gannagé [25] prepared dicyclohexyl-mercury by the action of sodium amalgam on bromocyclohexane; the mercury derivative forms needles of a camphor-like odor, melting at 139°. Mercury derivatives of

[24] *Ber.* 47, 3257 (1914).
[25] *J. Chem. Soc. Abs.* 120 (1), 472 (1921).

methylcyclohexane were similarly prepared from 4-bromomethylcyclohexane. Derivatives of the type RHgCl were made from dicyclohexylmercury by the action of benzoyl chloride or arsenic trichloride.

Some Simple Derivatives of Cyclohexane: An extensive review of the derivatives of cyclohexane is beyond the scope and purpose of the present volume but a brief description of some of the more important derivatives indicating the close parallelism in the chemistry of cyclohexane and normal hexane, and other examples of chemical behavior which are likely to prove of interest in connection with the chemical investigation of petroleum, are given.

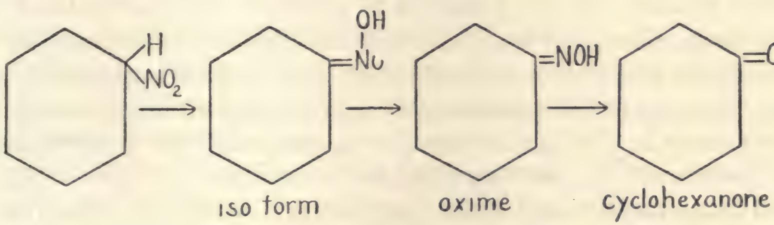
Cyclohexane is readily acted upon by dry chlorine, direct sunlight not being required. The monochloride, boiling-point 141.6°–142.6°, d $\frac{22^\circ}{0^\circ}$ 0.9976, is also readily prepared by the action of concentrated hydrochloric acid or PCl_3 on cyclohexanol. On treating with alkalies the chloride forms cyclohexene and when alcoholic caustic alkalies are employed a small proportion of cyclohexylethyl ether is formed; in fact, the behavior of the chloride closely parallels the behavior of the monochloro n. hexanes. Like the monochloropentanes and monochlorohexanes the cyclohexyl derivative is decomposed by passing over anhydrous barium chloride or alumina at 350°–450°, cyclohexene being formed almost quantitatively.[26] Another process for converting chlorocyclohexane to cyclohexene describes passing the chloride over lime at 350°–450° or over barium chloride at 300°–400°.[27] Fortey [28] decomposed the chloride by heating with quinoline and described the resulting *cyclohexene* as boiling at 82.3° d $\frac{4^\circ}{4^\circ}$ 0.8244, but Auwers [29] gives the following physical constants, boiling-point 83°–83.5° (760 mm.), d $\frac{15.6^\circ}{4^\circ}$ 0.8143, n_D 1.44921, M_D 27.03 (calculated M_D 27.24). Cyclohexene cannot be made satisfactorily from cyclohexanol by heating with anhydrous oxalic acid, the principal product being dicyclohexyl oxalate, but heating with potassium acid sulfate gives an 80 per cent yield of cyclohexene.[30] A small proportion of cyclohexyl ether, boiling-point 239°–240°, is also formed. The bromine and iodine derivatives are naturally more easily decomposed than the chlorides, but a double bond adjacent to the halogen stabilizes the substance as in the aliphatic se-

[26] Badische, Anilin n. Soda Fabr., *J. Chem. Soc. Abs. 1913* (1), 349.
[27] Schmidt, Hochschwender & Eichler, *Chem. Abs. 1917*, 1885.
[28] *J. Chem. Soc. 73*, 941 (1898).
[29] *Ann. 410*, 257 (1915).
[30] Willstätter & Hatt, *Ber. 45*, 1464 (1912).

ries. Usually the halogen derivatives have not been prepared from the hydrocarbon but from the alcohols. Thus cyclohexanol and concentrated hydriodic acid yield cyclohexyl iodide and quinite yields the corresponding 1.4 dihalogen derivatives.

When cyclohexane is chlorinated in the cold a mixture of chlorides is obtained. Two dichlorocyclohexanes are obtained, one boiling at 105.4°–106.4° (50 mm.) and the other distilling at 112.4°–113.4° (50 mm.); the former on prolonged boiling with alcoholic caustic potash yields a chlorocyclohexene. On distilling at atmospheric pressure the dichlorides decompose markedly. Continued chlorination yields tetrachlorocyclohexane, crystallizing from chloroform in long prisms melting at 173°.[31]

Cyclohexane is practically unacted upon by the usual nitrating mixture of nitric and sulfuric acids, but may be nitrated by heating in a sealed tube with dilute nitric acid according to the method discovered by Konowalow.[32] Its behavior in this respect is practically identical with that of n.hexane and the properties of the resulting nitrocyclohexane are quite different from the properties of nitrobenzene. On reduction with tin and hydrochloric acid, the corresponding amine is not formed but cyclohexanone or its condensation products are formed, evidently through the intermediate formation of the oxime of cyclohexanone,



Dinitro and trinitro derivatives of cyclohexane cannot be prepared by the nitration method noted above. Alkyl derivatives of cyclohexane, such as methyl or dimethylcyclohexane, containing a tertiary hydrogen atom are much more easily nitrated by Konowalow's method, the nitro group replacing the tertiary hydrogen atom. Like primary and secondary nitro derivatives of the aliphatic series, nitrocyclohexane is soluble in alkalies, evidently forming salts of the iso form whose structure is noted above. Nitro cyclohexane boils at 205.5°, d 20° 1.0616.

[31] Sabatier & Mailhe, *Compt. rend.* *137*, 240 (1903).
[32] *Compt. rend.* *121*, 652 (1895).

Nametkin[33] states that the yield of nitrocyclohexane is increased by nitrating the hydrocarbon with about three parts by weight of aluminum nitrate. Cyclohexane yields about 56 per cent of nitrocyclohexane together with cyclohexanone and dinitrodicyclohexyl, $C_{12}H_{20}(NO_2)_2$ melting at 216.5°.

Aminocyclohexane and other amino derivatives of the cyclohexanes differ markedly from the amines of the benzene hydrocarbons, particularly in their behavior when treated with nitrous acid. As noted above aminocyclohexane is best prepared by reduction of the oxime of cyclohexanone in alkaline solution or by catalytic hydrogenation by the Sabatier and Senderens method. Heating cyclohexanone or similar ketones with ammonium formate and reduction of the resulting formyl derivative to the amine has also occasionally been employed,[34] but reduction of the oxime generally gives much better yields. In the case of tertiary nitro compounds, such as 1-nitro-1-methylcyclohexane, reduction of the nitro group gives satisfactory yields since the tertiary nitro derivatives cannot rearrange to the iso forms with the resulting formation of oximes and ketones.

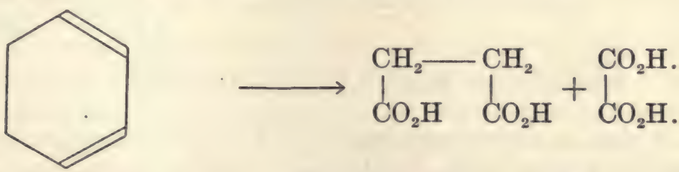
The aminocyclohexanes yield comparatively stable nitrites when treated with nitrous acid and on heating their aqueous solutions decomposition takes place with difficulty yielding the corresponding alcohol (yields usually very poor), and decomposition also proceeds in another manner with the formation of ammonia and unsaturated hydrocarbons. The latter reaction can be modified so as to serve admirably for the preparation of unsaturated hydrocarbons, particularly in cases where the resulting unsaturated hydrocarbon is easily rearranged or polymerized. For this purpose the amine is subjected to exhaustive methylation and the resulting alkylated ammonium hydroxide decomposed by gentle heating, a method mentioned in connection with cyclobutene and which warrants more extensive applications in research. Decomposition of the phosphates of amines of this type by heating has also been employed for converting the amines to unsaturated hydrocarbons.[35]

The method of reducing the oximes to amines has been employed for the preparation of the 1.3-diamine and 1.4-diamine, the oximes being prepared from the corresponding ketones. The 1.2-diamine has been prepared from anthranilic acid which can be best reduced by the

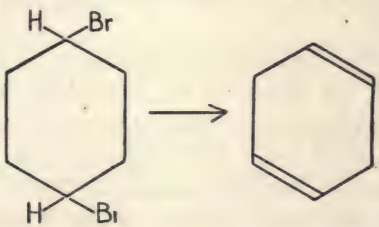
[33] *J. Russ. Phys.-Chem. Soc. 42,* 581 (1910).
[34] Leuchart & Bach, *Ber. 20,* 104 (1887).
[35] Harries, *Ber. 34,* 300 (1901).

method of Ipatiev or by sodium and amyl alcohol.[36] The amide of the reduced acid may then be converted to the diamine in the usual manner by bromine and alkali.[37]

The *cyclohexadienes* have been of considerable interest on account of their close relation to benzene. A cyclohexadiene boiling at 84°–86° was first made by Baeyer [38] and the same laborious methods of preparation were later employed by Crossley.[39] A product evidently identical with Baeyer's and having the same boiling-point was made by Markownikow by decomposing chlorinated cyclohexane isolated from Russian petroleum.[40] Fortey reported a cyclohexadiene boiling at 81°–82° [41] and Harries and Antoni [42] obtained a product of the same boiling-point, 81.5°, by the decomposition of the phosphate of 1.4-diaminocyclohexane. From 1.2-dibromocyclohexane Crossley [43] also obtained the low-boiling product and, from its method of preparation and the fact that oxidation by nitric acid yielded oxalic and succinic acids, concluded that the low-boiling product was 1.3-cyclohexadiene.

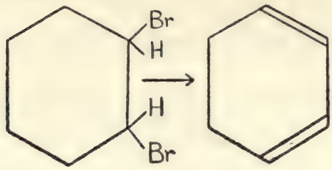


Zelinsky and Gorsky [44] obtained the high-boiling hydrocarbon from 1.4 dibromocyclohexane and the low-boiling one from 1.2 dibromocyclohexane. Both hydrocarbons form different and characteristic dibromides and tetrabromides.



$\Delta^{1.4}$ *cyclohexadiene*
B.-P. 85°–86°

[36] Einhorn & Meyerburg, *Ber.* **27**, 2466 (1894).
[37] Einhorn & Bull, *Ber.* **29**, 964 (1896); *Ann.* **295**, 187.
[38] *Ber.* **25**, 1840 (1892).
[39] *J. Chem. Soc.* **85**, 1410 (1904).
[40] *Ann.* **302**, 30 (1898).
[41] *J. Chem. Soc.* **73**, 945 (1898).
[42] *Ann.* **328**, 93, 105 (1903).
[43] *Loc. cit.*
[44] *Ber.* **41**, 2479 (1908).



$\Delta^{1,3}$ *cyclohexadiene*
B.-P. 81.5°

Although the evidence of the existence of the two isomeric hexadienes is quite clear some doubt as to their constitution has been expressed on account of the fact that neither of the hexadienes shows the exaltation of the molecular refraction which two conjugated double bonds were supposed always to show. However, Auwers has shown that cyclopentadiene, which must contain conjugated double bonds, and cycloheptadiene, containing conjugated double bonds, do not show any exaltation and the conjugated cyclic trienes show only very slight exaltation.[45] The agreement with the calculated value of $\Delta^{1,3}$-cyclohexadiene is in fact within the experimental error, if we accept the more recent determinations of Harries [46] and of Willstätter and Hatt.[47]

	EM_α	EM_D
Harries	0.05	0.09
Willstätter and Hatt	0.00	0.02

A similar discrepancy between the observed refractivity and the expected exalted value due to conjugation of double bonds confused for a time the question of the constitution of the substituted cyclohexadiene, α-terpinene (q. v.). The determination of the constitution of such hydrocarbons has been particularly difficult on account of the ease with which the double bonds shift their positions. Thus the preparation of pure α- or γ-terpinene, α- or β-phellandrene, and terpinolene is practically impossible.

The cyclohexadienes show a very marked tendency to oxidize to benzene (or its homologues), for example, the oxidation of the terpinenes to cymene. Also cyclohexadiene (probably a mixture of the two isomers) is converted to benzene by dehydrogenation in the presence of nickel at the remarkably low temperature of 180°.[48] Dilute acids very frequently cause shifting of double bonds when a more stable substance can result, and a double bond in a side chain frequently shifts to the ring. Thus 2-phenyl and 2-propyl-$\Delta^{2,5,8,(9)}$-men-

[45] For a fuller discussion of the refractivity of cyclic and acyclic hydrocarbons see the chapter on physical properties.
[46] *Ber.* *45,* 809 (1912).
[47] *Ber.* *45,* 1647 (1912).
[48] Boeseken, *Rec. trav. chim.* *37,* 255 (1918).

thatriene are quickly converted to the isomeric benzene derivatives by warming with 3 per cent hydrochloric acid.[49]

Conjugated dienes react with concentrated sulfuric acid with almost explosive violence, with tar formation and reduction of the acid, a behavior frequently noted on refining crude benzene containing cyclopentadiene and cyclohexadiene and this energetic action is particularly marked when the crude benzene has been manufactured from oil, as in Pintsch gas "hydrocarbon" or carburetted water gas tar. Under the same conditions that amylene and such simple olefines give good yields of the alcohols (i. e., by treating with ordinary sulfuric acid in the cold and diluting with water) the conjugated diolefines yield only tar.

Cyclohexanol: This alcohol promises to become a common commercial product[50] as a result of the development of methods of catalytic hydrogenation, being readily prepared from phenol. Cyclohexanol has a camphor-like odor, boils at 160.9°, melts at 23°, d $\frac{37°}{4°}$ 0.9397, n_D 1.46055.[51] It is sparingly soluble in water but is hygroscopic, a little water lowering the freezing-point, a eutectic point being noted at —47.4°, the liquid containing 4.97 per cent of water at that point.[52] The acetate resembles amyl acetate and while it has no very marked physiological action, the narcotic action of the vapors is about three times greater than the same property of amyl acetate.[53] The naphthylurethane[54] melts at 139°–140°.

When phenol is reduced with hydrogen over active nickel at 160°–170°, the nickel having been reduced from the oxide at 300°, the product is chiefly cyclohexanol together with a little unchanged phenol and a little cyclohexanone. Holleman[55] removed the cyclohexanone by condensing it with benzaldehyde in the presence of alkali. When cyclohexanol is passed over copper, with a little air, at 280° cyclohexanone

[49] Klages, *Ber. 40,* 2360 (1907).

[50] The use of cyclohexanol in soap is said to enable one to incorporate solvents such as benzene, tetraline, chlorinated solvents and the like in the soap and also facilitates the manufacture of soaps containing phenolic insecticides. Its use as a solvent for rubber in reclaiming rubber is mentioned in German Patent 366,146. Like fusel oil and amyl acetate, cyclohexanol and its acetate are of value as solvents for nitro cellulose, such solutions being capable of considerable dilution with the common hydrocarbon solvents, gasoline, benzene, etc. The use of cyclohexanol and cyclohexanone in the manufacture of celluloid has been patented by Raschig, German Pat. 174,914 (1905).

[51] Auwers, *Ann. 410,* 257 (1915).

[52] Forcrand, *Compt. rend. 155,* 118 (1912).

[53] Lehmann, *Chem. Abs. 1913,* 2432.

[54] Neuberg, *Bioch. Z. 27,* 339.

[55] *Rec. trav. chim. 24,* 19 (1905); Brochet [*J. Soc. Chem. Ind. 32,* 1031 (1913)] used nickel and hydrogen at 120°-180° and 10 to 15 kilograms per sq. cm. pressure.

is produced in good yields. Sabatier and Senderens[56] reduced phenol at a higher temperature and obtained a mixture of cyclohexanone and cyclohexanol, from which they prepared cyclohexanol by passing again over the catalyst with hydrogen at a lower temperature, 140°–150°, and prepared nearly pure cyclohexanone by passing the mixture over copper at 330°. Cyclohexanol is readily oxidized to cyclohexanone by chromic acid, under the same conditions that aliphatic secondary alcohols are oxidized to the corresponding ketones.

Cyclohexane-1.2-diol, melting-point 99°–100°, is formed when cyclohexene is oxidized by cold dilute permanganate in the usual manner. *Cyclohexane-1.3-diol,*[57] melting-point 65°, is produced by the catalytic hydrogenation of resorcinol in the presence of nickel at 130°. It is easily soluble in water and alcohol, does not reduce Fehlings' solution or give a color with ferric chloride. *Cyclohexane-1.2.3-triol* was also obtained by the catalytic hydrogenation of pyrogallol, the triol forming very hygroscopic crystals melting at 67°. Cyclohexane-1.3.5-diol, made by reducing phloroglucine with sodium amalgam, melts at 184°. *Cyclohexane-1.4-diol,* also called *quinite* can be obtained by catalytic hydrogenation of hydroquinone and was also prepared by Baeyer by reducing cyclohexane-1.4-dione with sodium amalgam. It was named quinite on account of its relation to benzoquinone, which it yields when oxidized by chromic acid. Two other hydroxyl derivatives of cyclohexane may be mentioned on account of their interest to biochemistry, i. e., *quercite,* cyclohexane-1.2.3.4.5-pentol, and *inosite,* cyclohexane-1.2.3.4.5.6-hexol. Quercite is known in two forms $[\alpha]_D + 24.16°$, melting-point 235°, and $[\alpha]_D - 73.9°$, melting-point 174°. The chemical behavior of quercite and inosite is very closely parallel to the behavior of sorbite, rhamnite, etc. Both substances have been known for a long time and their chief interest in connection with a discussion of the chemistry of the hydrocarbons is that ring closing makes such slight differences in their chemical properties as compared with the alcohols of the methyl pentose and hexose series. Quercite yields a pentacetyl derivative melting at 125°, an explosive pentanitrate and an amorphous pentaphenyl carbamate. Inosite yields a hexacetate melting at 212° and a very explosive hexanitrate. A monomethyl ether of inosite has been reported in a caoutchouc (gutta-percha ?) from Borneo and a dimethyl ether in another

[56] *Compt. rend. 137,* 1025 (1903).
[57] Sabatier & Mailhe, *Compt. rend. 146,* 1193 (1908).

specimen of caoutchouc.[58] The resin of the California pine, *Pinus lambertiana*, also contains a monomethyl ether of d-inosite.[59] This ether, pinite, has been found in other plant secretions, tastes very sweet, melts at 186°, and following the general behavior of such ethers, is readily split by warming with concentrated hydriodic acid, to methyl iodide and the alcohol.

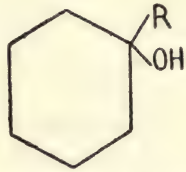
THE PHYSICAL PROPERTIES AND LITERATURE REFERENCES OF THE CYCLOHEXANOLS

Name	*B.-P.*	$d\frac{20°}{4°}$	$n\frac{20°}{D}$	*References*
Cyclohexanol	160.9°	0.949	1.4659	1
Methylcyclohexanol-(1)	156. °–158. °	0.924	1.4585	1
Methylcyclohexanol-(2)	168. °	0.928	1.463	2
Methylcyclohexanol-(3)	174. °	0.917	1.458	3
Methylcyclohexanol-(4)	173. °	0.919	1.458	4
1.3-Dimethylcyclohexanol-(1)	169. °	0.903	1.455	5
1.4-Dimethylcyclohexanol-(1)	170. °	0.909	1.457	5, 6
2.2-Dimethylcyclohexanol-(1)	177. °	0.922	1.464	7
3 3-Dimethylcyclohexanol-(1)	185. °	0.909	1.459	8
4.4-Dimethylcyclohexanol-(1)	186. °	0.925	1.463	9
2.4-Dimethylcyclohexanol-(1)	176.5°	0.908	1.4562	10
2.5-Dimethylcyclohexanol-(1)	178.5°	0.904	1.4532	10
2.6-Dimethylcyclohexanol-(1)	174.5°–175.5°	0.924	1.4628	11
3.4-Dimethylcyclohexanol-(1)	189. °	0.904	1.4562	10
3.5-Dimethylcyclohexanol-(1)	187. °	0.898	1.453	12
1.3.5-Trimethylcyclohexanol-(1)	181. °	0.886	1.453	13
3.3.5-Trimethylcyclohexanol-(1)	200. °	0.897	1.453	12
2.2.5-Trimethylcyclohexanol-(1)	187. °	0.900	1.459	14
2.2.6.6-Tetramethylcyclohexanol-(1)	195. °–197. °	0.897	1.4537	15
2.2.5.5-Tetramethylcyclohexanol-(1)	202. °	0.902	1.462	16

1 Zelinsky, *Ber. 34*, 2800 (1901); Auwers, *Ann. 410*, 309 (1915).
2 Wallach, *Ann. 329*, 375 (1903); Murat, *Chem. Zentr. 1909* (2), 851.
3 Zelinsky, *Ber. 30*, 1534 (1897); Haller and March, *Chem. Zentr. 1905* (2), 325; Sabatier and Mailhe, *Chem. Zentr. 1905* (1), 742.
4 Sabatier and Mailhe, *Chem. Zentr. 1907* (1), 1096; Auwers, *Ann. 410*, 309 (1915).
5 Sabatier and Mailhe, *Chem. Zentr. 1905* (2), 483.
6 Wallach, *Ann. 396*, 266 (1913).
7 Auwers and Lange, *Ann. 401*, 319 (1913); Meerwein, *Ann. 405*, 144 (1914).
8 Perkin, Sr., *J. Chem. Soc. 87*, 1493 (1905); Auwers and Lange, *Ann. 401*, 314 (1913).
9 Auwers and Lange, *loc cit.*
10 Sabatier and Mailhe, *Chem. Zentr. 1906* (1), 1248.
11 Haller, *Chem. Zentr. 1913* (2), 1144.
12 Knoevenagel, *Ann. 297*, 182 (1897); Auwers, *Ann. 410*, 311 (1915).
13 Wallach and Schlubach, *Ann. 396*, 284 (1913).
14 Wallach, *Ann. 329*, 87 (1903); Auwers, *Ber. 41*, 1814 (1908).
15 Haller, *Chem. Zentr. 1913* (2), 41.
16 Auwers and Lange, *Ann. 409*, 178 (1915).

[58] Flint & Tollens, *Ann. 272*, 288 (1893).
[59] Wiley, *J. Am. Chem. Soc. 13*, 228 (1891).

A great many alkyl derivatives of cyclohexanol are known, the simpler ones being readily made by catalytic hydrogenation of the cresols, by the Grignard reaction on cyclohexanone and other well-known methods. As in the aliphatic series the secondary alcohols are not easily decomposed to unsaturated hydrocarbons but tertiary alcohols of the type



yield unsaturated hydrocarbons very readily.

Cyclohexanone: On account of the very great value of this ketone as a material for the synthesis of a very large number and variety of hydrocarbons, it will be briefly described. Its best method of preparation has already been described in connection with cyclohexanol. Its chemical behavior closely parallels that of the aliphatic ketones. Pure cyclohexanone boils at 156.6°–156.8° $d\frac{15.3°}{4°}$ 0.9503, n_D 1.45261.[60] It may be characterized by the phenylhydrazone melting at 74°–77° and the condensation products with benzaldehyde $C_6H_5CH = (C_6H_8O)$ melting at 53° and the dibenzylidene compound $C_6H_5CH = (C_6H_6O) = CH.C_6H_5$ melting at 117°.[61] The ketone, like cyclopentanone, is condensed by sodium ethylate or by gaseous hydrogen chloride to cyclohexylidenecyclohexanone and a dicyclohexylidenecyclohexanone. The ring is not easily broken but in direct sunlight in dilute alcohol solution capronic acid and Δ^5 hexene aldehyde are formed, and the oxime is converted by concentrated sulfuric acid to the iso-oxime, or ε-caprolactam. With an excess of bromine in the cold it yields a tetrabromide melting at 119°, but when brominated hot the chief product is 2.4.6-tribromophenol.[62]

Methylcyclohexane occurs in Russian [63] and Galician [64] petroleum. Galician petroleum appears to be midway between Russian petroleum and oils of the Pennsylvania type. The presence of methylcyclohexane in Russian petroleum was regarded as "probable" by Young. It also

[60] Auwers, *Ann.* *410,* 257 (1915).
[61] Wallach, *Goettingen Nachr.* *1907,* 402; *Ber.* *40,* 71.
[62] Bodroux & Taboury, *Compt. rend.* *154,* 1509 (1912).
[63] Milkowski, *J. Russ. Phys.-Chem. Soc.* *17,* 37 (1885); Zelinsky, *Ber.* *30,* 1532 (1897).
[64] Skowronski, *Chem. Abs.* *1920,* 3523.

occurs in rosin spirit[65] and can readily be prepared by the catalytic hydrogenation of toluene. Reduction of cycloheptanol by heating with concentrated hydriodic acid causes a rearrangement of the carbon structure giving methyl cyclohexane as the reduction product.

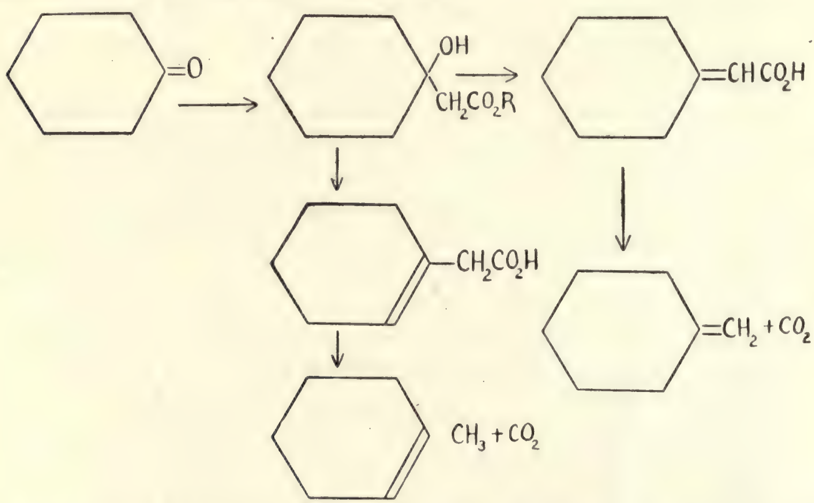
When treated with bromine and aluminum bromide the principal product is pentabromotoluene, melting at 282°, and this fact can be used for detecting the presence of methyl cyclohexane in gasoline, after proper fractional distillation. When methylcyclohexane is nitrated by Konowalow's method using nitric acid, Sp. Gr. 1.20, the yield of nitro derivatives is about 58 per cent, but Nametkin[66] reports that nitration by aluminum nitrate gives about 72 per cent of nitrated products. The tertiary nitro derivative may be separated from the primary and secondary derivatives by the solubility of the latter two types in alkali. 1.1-Nitromethylcyclohexane is a liquid distilling at 109–°110° (40 mm.), $d\frac{0°}{4°}$1.0547 and may be reduced by tin and hydrochloric acid to the amine boiling-point, 143° (744 mm.). The 1.3-nitromethylcyclohexane distills at 119°–120° (40 mm.), $d\frac{0°}{4°}$ 1.0547; cyclohexylnitromethane, $C_6H_{11}.CH_2NO_2$, is also formed. Oxidation of methylcyclohexane by nitric acid yields a mixture of adipic, succinic, oxalic, glutaric and pyrotartaric acids.

The chlorination of methylcyclohexane yields, of the monochlorides, about 60 per cent 1-methyl-3-chlorocyclohexane and about 40 per cent of the 1.2-derivative. This was shown by forming the magnesium derivatives with the monochlorides passing oxygen into the ethereal Grignard solution, and examining the resulting alcohols. Cyclohexylmethyl chloride, $C_6H_{11}.CH_2Cl$, made from the corresponding carbinol, boils at 166° (760 mm.) without appreciable decomposition; 2-chloromethylcyclohexane boils at 156° with slight decomposition; 3-chloromethylcyclohexane distills at 157° and 4-chloromethylcyclohexane distills at 158°, also decomposing appreciably.[67]

Methyl Cyclohexenes: Of the three methyl cyclohexenes Δ^1-methyl cyclohexene is the most stable, the other two isomers being readily converted to the Δ^1 hydrocarbon by heating with dilute acids. The Δ^1 hydrocarbon is also present in the mixture of hydrocarbons obtained by decomposing methylcyclohexanol-(3) or methylcyclohexanol-(4) with phosphorus pentoxide or zinc chloride. Decomposition of 1.1 or

[65] *Ann. chim. phys.* (6) *1*, 229 (1884).
[66] *J. Russ. Phys.-Chem. Soc. 42*, 691 (1910).
[67] Sabatier & Mailhe, *Compt. rend. 140*, 840 (1905).

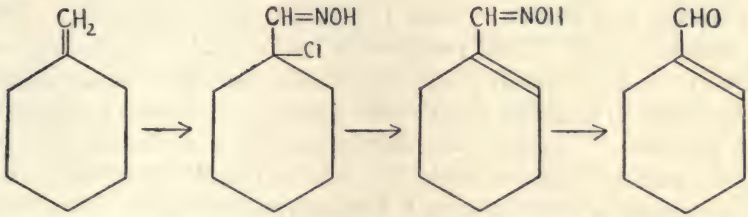
1.2-methylcyclohexanol yields the Δ^1 hydrocarbon. Wallach [68] prepared it by treating cyclohexanone with methyl-magnesium iodide and decomposing the tertiary alcohol by zinc chloride. Its boiling-point, 111°–112°, is several degrees higher than the isomeric methenecyclohexane prepared by Wallach by distilling and decomposing cyclohexene acetic acid. The Δ^1 hydrocarbon yields a glycol, by permanganate oxidation, melting at 67°. When 1.2 methylcyclohexanol is decomposed by Ipatiev's method, passing the vapors over heated alumina at 350°, a mixture of methylcyclohexenes, distilling from 96°–100°, is formed, but when a mixture of alumina and copper oxide is used, the reaction takes place smoothly at 240° and the product is nearly pure Δ^1-methylcyclohexene.[69] By condensing cyclohexanone and bromoacetic ester in the presence of zinc, Wallach [70] made cyclohexanolacetic acid which on decomposing with bisulfate or P_2O_5 yields mainly Δ^1-cyclohexene-acetic acid but by heating with acetic anhydride yields mainly $\Delta^{1(7)}$-cyclohexeneacetic acid, a reaction frequently employed for the synthesis of methene derivatives in the cyclohexane and cyclopentane series. Distillation of the unsaturated acids yields the hydrocarbons, as indicated below,



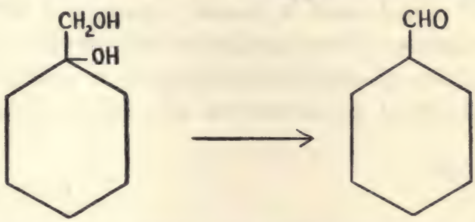
Methenecyclohexane [71] boils at 103°, d_{19} 0.8020, n_D 1.4499. It readily absorbs hydrogen chloride, forming an unstable chloride boiling

[68] *Ann.* *359*, 287 (1908).
[69] *Ber.* *43*, 3383 (1910); *J. Russ. Phys.-Chem. Soc.* *44*, 1675 (1913).
[70] *Ann.* *353*, 288 (1906).
[71] Wallach, *Ann.* *365*, 262 (1909); Favorsky & Borgmann, *Ber.* *40*, 4863.

at 151°–152°. It is easily converted to Δ^1-methylcyclohexene by alcoholic sulfuric acid and on hydrating by dilute sulfuric acid yields the tertiary alcohol 1.1-methylcyclohexanol. Permanganate oxidation yields cyclohexanone and a glycol melting at 67°–77°. Its nitrosochloride may be converted into the nitrolpiperidide, useful for identification or HCl may be removed by heating with sodium acetate in acetic acid to give an aldoxime (a very general reaction of nitrosochlorides, giving an aldoxime or ketoxime). Hydrolysis of the aldoxime yields Δ^1-cyclohexene aldehyde, an aldehyde having an odor greatly resembling benzaldehyde. Since these reactions are widely applicable and have in fact been frequently employed, they are noted here,



The glycol is readily converted to the saturated cyclohexyl aldehyde by the action of dilute acids, also a very general reaction, and having its parallel in the behavior of the 1.2-glycols of the aliphatic series



Unlike benzaldehyde, cyclohexyl aldehyde polymerizes very easily to the dimeride $(C_7H_{12}O)_2$ and with acids the substance (trimeride ?) $(C_7H_{12}O)_3$ is formed.

Δ^3-*Methylcyclohexene*, boiling-point 103°, may be obtained by heating and decomposing the acid phthalic ester or methyl xanthogenate of methylcyclohexanol(3) or by decomposing the iodide by alcoholic caustic potash or dimethyl aniline. From optically active methylcyclohexanol (3) Zelinsky [72] obtained an optically active hydrocarbon by decomposing the iodide. The hydrocarbon, the constitu-

[72] *Ber.* 35, 2488 (1902).

tion of which was not proven, varied according to the method of preparation, the hydrocarbon obtained by caustic potash having the highest rotation,

(1) by alcoholic KOH,—boiling-point 103°–103.5°, $[\alpha]_D + 81.4°$

(2) by dimethyl aniline, boiling-point 105°–106 °, $[\alpha]_D + 48.3°$

When Δ^3-methylcyclohexene is treated with sulfuric acid (1 volume water to two volumes of acid) the principal product is the dimeride, $C_{14}H_{24}$, and more dilute acid (1:1 by volume) converts it to a mixture of the Δ^1 and Δ^2 isomers and alcohols, among which methylcyclohexanol(3) were identified.[73]

1.1 Dimethylcyclohexane: This hydrocarbon has been synthesized by Crossley and Renouf,[74] from 1.1-dimethyldihydroresorcin. Zelinsky and Lepesckin[75] had prepared a hydrocarbon which they considered to be 1.1-dimethylcyclohexane from laurolene and isolaurolene but the work of Crossley and Renouf shows that Zelinsky's conclusions were incorrect. Crossley and Renouf treated 1.1-dimethylcyclohexanol(3) with hydrogen bromide in acetic acid and reduced the bromide with zinc dust in acetic acid to 1.1-dimethylcyclohexane. The hydrocarbon is stable to bromine and permanganate in the cold and is slowly oxidized by fuming nitric acid to ββ-dimethyladipic acid. When the above bromide(3) is treated with alcoholic caustic potash *1.1-dimethyl-Δ^3-cyclohexene* is formed, apparently not contaminated with the Δ^2-isomeride. The unsaturated hydrocarbon has a turpentine like odor and yields ββ-dimethyladipic acid on oxidation by permanganate. The physical properties of the two hydrocarbons are as follows,

	B.-P.	$d\frac{15°}{15°}$
1.1-dimethylcyclohexane	102°	0.7864
1.1-dimethyl-Δ^3-cyclohexene	117°–117.5°	0.8040

Zelinsky's hydrocarbon boils at 111.5°–114°, $d\frac{17}{4}$ 0.7686, and on oxidation does not yield ββ-dimethyladipic acid. The physical properties of 1.1-dimethylcyclohexane prepared from 1.1-dimethylcyclohexane-3-one, by reduction to the alcohol, and conversion of the latter to the

[73] Markownikow, *J. Russ. Phys.-Chem. Soc. 35*, 1049 (1903).
[74] *J. Chem. Soc. 87*, 1487 (1905) ; *89*, 27 (1906).
[75] *Ann. 319*, 303 (1901) ; *J. Russ. Phys.-Chem. Soc. 33*, 549 (1901).

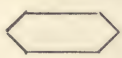
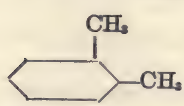
unsaturated hydrocarbon followed by catalytic hydrogenation were, boiling-point 118.5°, $d\frac{20°}{4°}$ 0.7825, $n\frac{20°}{D}$ 1.4289.[76]

Zelinsky and Lepeschkin[77] later confirmed the work of Crossley and Renouf by the synthesis of 1.1-dimethylcyclohexane in another manner (from β-methyl-Δβ-heptone-ζ-one) and noted the following: boiling-point 119-2°–119.7°, $d\frac{16°}{4°}$ 0.7843, $n\frac{16°}{D}$ 1.4320. When 1.1-dimethylcyclohexane is brominated in the presence of aluminum bromide one of the methyl groups goes to the para position, resulting in a *para*-xylene derivative.

Auwers[78] has prepared a series of methyl derivatives of cyclohexane. The method of preparation most frequently employed was the catalytic hydrogenation of phenols, conversion of the resulting secondary alcohols to iodides and reduction of the latter by zinc dust and acetic acid. Also tertiary alcohols, formed by treating cyclohexanone derivatives with magnesium methyl iodide, were converted to the corresponding chlorides by the action of phosphorus trichloride and the resulting chlorides reduced to the saturated hydrocarbon by sodium in moist ether. A summary of the physical properties of the methyl derivatives of cyclohexane, as determined by Auwers is given in the following table.

Alkyl Derivatives of Cyclohexane:

I. Methyl Derivatives.

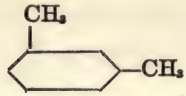
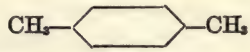
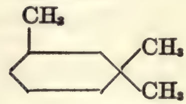
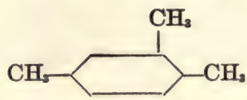
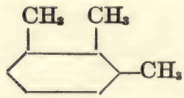
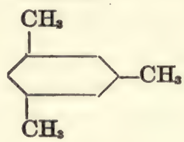
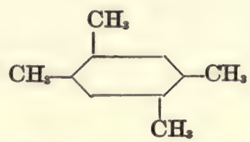
Name	*Structure*	*B.-P.**	$d\frac{20°}{4°}$	$n\frac{20°}{4°}$
Cyclohexane		80.5°	0.778	1.427
Methylcyclohexane		101. °	0.771	1.423
1.1-dimethylcyclohexane		120. °	0.781	1.430
1.2-dimethylcyclohexane		123. °	0.779	1.429

* The above data show that the density decreases as the methyl groups are separated more widely from each other.

[76] Gadaski & Ssorokina, *Chem. Ztg. 37*, 725 (1913).

[77] *J. Russ. Phys.-Chem. Soc. 45*, 613 (1913).

[78] *Ann. 420*, 88 (1919).

1.3-dimethylcyclohexane [79]		119. °	0.771	1.425
1.4-dimethylcyclohexane		120. °	0.769	1.424
1.1.3-trimethylcyclohexane		138. °	0.790	1.436
1.2.4-trimethylcyclohexane		140. °	0.778	1.429
1.2.3-trimethylcyclohexane [80]		149.6°–150°	..	..
1.3.5-trimethylcyclohexane		138. °	0.772	1.429
1.2.4.5-tetramethylcyclohexane		161. °	0.785	1.434

The boiling-points and densities of other alkyl derivatives of cyclohexane are given in the following table.

ALKYL DERIVATIVES OF CYCLOHEXANE II.

Name	*B.-P.*	*Density,* $\frac{20°}{4°}$	*References*
Ethylcyclohexane	130°	0.7772	1
1.2-Methylethylcyclohexane	151°	0.784	2
n.Propylcyclohexane	156°	0.7865	3
Tertiarybutylcyclohexane	166°–167°	0.8305 $\frac{16°}{4°}$	4
1.3-Methylethylcyclohexane	145°–146°	0.8320	5
1.3-Methylpropylcyclohexane	164°–165°	.....	5
1.2-Methylisopropylcyclohexane [o-menthane]	171°	0.8135 $\frac{21°}{0°}$	6
1.3-Methylisopropylcyclohexane [m-menthane]	166°–167°	0.7965 $\frac{24°}{0°}$	6

[79] Zelinsky, *Ber. 35,* 2677 (1902), gives the following, boiling-point 119.5-120°, d$\frac{26°}{4°}$ 0.7661. Zelinsky prepared the hydrocarbon by converting 1.3-dimethyl cyclohexanol (1) to the iodide and reducing it with zinc in acetic acid.

[80] Treppmann & Krollpfeiffer, *Ber. 48,* 1226 (1915).

1.4-Methylisopropylcyclohexane [p-menthane] ...	167°–168°	$0.8028\frac{25°}{0°}$	6
2-Cyclohexyl-2-methylbutane $C_6H_{11}.C(CH_3)_2C_2H_5$	191°–192°	$0.8226\frac{16°}{4°}$	4
2-Cyclohexyl-2-methylpentane	206°–207°	$0.8372\frac{16°}{4°}$	4
3-Cyclohexyl-3-methylpentane	207°–208°	$0.8310\frac{16°}{4°}$	4
3-Cyclohexyl-3-ethylpentane	222°–223°	$0.8388\frac{16°}{4°}$	4
2-Cyclohexyl-2.4-dimethylpentane	220°–221°	$0.8304\frac{16°}{4°}$	4
3-Cyclohexyl-3-methylhexane	224°–226°	$0.8406\frac{16°}{4°}$	4
1-Methyl-2-isoamylcyclohexane	204°	$0.812\frac{17°}{4°}$	7

1 Sabatier and Senderens, *Compt. rend. 132*, 210, 556 (1901).
2 Murat, *Ann. chim. phys.* (8) *16*, 108 (1909).
3 Kursanoff, *Ber. 34*, 2035.
4 Halse, *J. prakt. Chem.* (2) *92*, 40 (1915). The hydrocarbons described by Halse were made by Willstätter's method of catalytic hydrogenation.
5 Mailhe and Murat, *Bull. soc. chim. 7*, 1083 (1910). Zelinsky, *Ber. 35*, 2677 (1902), gives the boiling-point 148°-149°, $d\frac{17°}{4°}$ 0.7896.
6 Sabatier and Murat, *Compt. rend. 156*, 184.
7 Murat, *Ann. chim.* (8) *16*, 108 (1909).

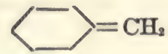
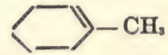
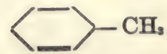
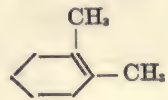
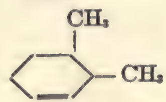
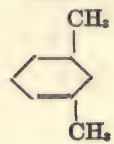
Of the hydrocarbons noted in the above tables, cyclohexane, methylcyclohexane, 1.3-dimethylcyclohexane and 1.3.4-trimethylcyclohexane have been reported in the lighter fractions of Russian petroleum, and the methyl, propyl, 1.3-dimethyl and 1.4-dimethyl derivatives have been reported in rosin oil. The method of identifying alkyl cyclohexanes by brominating in the presence of aluminum bromide to benzene derivatives which are supposed to retain the alkyl groups in the same relative positions as they occurred in the original cyclohexane hydrocarbon, is open to the objection that profound alteration of the carbon structure of the hydrocarbon has frequently been observed in the presence of aluminum bromide; thus 1.1-dimethylcyclohexane gives a bromide derivative of *para-xylene.* The same objection could be made to an attempt to convert the alkyl cyclohexane to the corresponding alkyl benzenes by dehydrogenation over nickel at about 300°. In view of the extreme difficulty of separating such hydrocarbons from petroleum by fractional distillation, to which difficulty Young has called attention, and the equally great difficulties and uncertainties of identifying them by chemical means (conversion to benzene derivatives or oxidation to known acids, etc.), it is quite

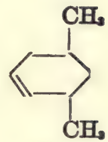
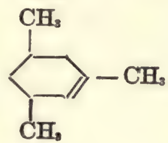
probable that many of the cyclic hydrocarbons reported to have been identified in Russian petroleum have been so reported on faulty or insufficient evidence.

Although a fair number of alkyl derivatives of cyclohexane are known, very little is known of their chemical behavior; for example, to concentrated sulfuric acid, nitric acid, chromic acid and the like. Even in the case of the menthanes, it is not known in what positions bromine enters on bromination and whether or not the tertiary hydrogen atoms are reactive to sulfuric acid or are easily oxidized. In view of the very large losses which result on treating petroleum distillates with sulfuric acid, it would be desirable to know whether the different types of substituted cyclohexanes, bicyclic and polycyclic hydrocarbons of different types, saturated in the sense that no double bonds are present, are resistant to air oxidation, resinification, destruction by concentrated sulfuric acid, etc.

The Substituted Cyclohexenes follow very generally the chemical behavior noted in the so-called terpene series. Only in comparatively recent years has it been realized that the chemistry of these hydrocarbons occurring in nature cannot be dissociated in any way from the chemistry of the simple derivatives of cyclopentane, cyclohexane and cycloheptane. The boiling points, densities and refractive indices of a number of unsaturated hydrocarbons of this series are given in the following table.

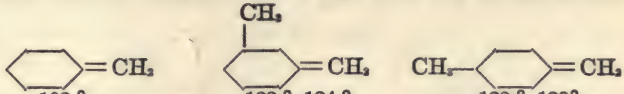
UNSATURATED HYDROCARBONS OF THE CYCLOHEXANE SERIES.

Structure and Name		B.-P.	Density	n_D	References
Methenecyclohexane		103. °	$0.8020\frac{19°}{4°}$	1.4499	1
		101.2°–102.0°	$0.8072\frac{13.8°}{4°}$	1.4534	2
Δ¹-methylcyclohexene		111. °–112. °	0.811	1.4496	3
Δ³-methylcyclohexene		103. °	$0.7937\frac{27°}{4°}$	.....	4
1.1-dimethyl-Δ³-cyclohexene		117. °–117.5°	$0.8040\frac{15°}{15°}$	.....	5
1.2-dimethyl-Δ¹-cyclohexene		136. °–137.5°	$0.824\frac{20°}{4°}$	1.460	6
1.2-dimethyl-Δ³-cyclohexene		124. °	$0.807\frac{20°}{4°}$	1.444	
1.3-dimethyl-Δ³-cyclohexene		124. °–126. °	$0.7998\frac{22.6°}{4°}$	1.4453	2

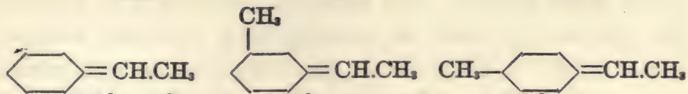
1.3-dimethyl-Δ^4-cyclohexene		126. °–127. °	$0.797\frac{21.1°}{4°}$	1.4436	2
1.4-dimethyl-Δ^1-cyclohexene		127. °–129. °	$0.8000\frac{20°}{4°}$	1.4451	7
1-methyl-4-methene-cyclohexane		122. °	$0.7920\frac{20°}{4°}$	1.445	7
1.3.5.-trimethyl-Δ^1-cyclohexene		140.5°–142. °	$0.8025\frac{14.3°}{4°}$	1.44909	2
1.2.5-trimethyl-Δ^4-cyclohexene		145. °	0.805	1.448	2
1.2.4.5.-tetramethyl-Δ^4-cyclohexene		166. °	0.817	1.457	2

1 Wallach, *Ann. 365*, 262 (1909).
2 Auwers, *Ann. 410*, 257 (1915).
3 Wallach, *Ann. 359*, 287 (1908).
4 Zelinsky, *Ber. 35*, 2493.
5 Crossley and Renouf, *J. Chem. Soc. 87*, 1487 (1905).
6 Meerwein, *Ann. 405*, 150 (1914).
7 Wallach, *Ann. 396*, 266; *397*, 190.

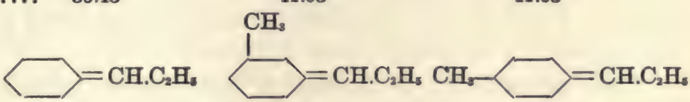
Wallach[81] tabulates the physical properties of a series of cyclohexane derivatives each of which contains a semicyclic double bond, as follows,



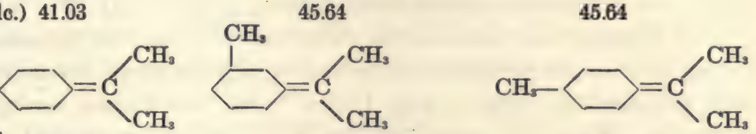
Boiling-point	102.°	123.°–124.°	122.°–123°
d	0.8025	0.798	0.7925
M_D	32.15	36.95	36.93
M_D (calc.)	31.83	36.43	36.43



Boiling-point	137.°–138.°	153.°	156.°
d	0.823	0.813	0.8125
M_D	36.82	41.65	41.65
M_D (calc.)	36.43	41.03	41.03



Boiling-point	157.°–158.°	170.°–173.°	172.°–174.°
d	0.821	0.814	0.815
M_D	41.60	46.35	46.28
M_D (calc.)	41.03	45.64	45.64



Boiling-point	160.°–161.°	173.°–175.°	172.°–174.°
d	0.836	0.825	0.831
M_D	41.56	46.25	45.88
M_D (calc.)	41.03	45.64	45.64

1.2-Dimethyl-Δ^1-Cyclohexene is of special interest since Meerwein[82] discovered that it is smoothly formed by the dehydration of the cyclopentane derivative 1-methyl-1-α-hydroxyethylcyclopentane.

$$\begin{array}{l} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{array} > C < \begin{array}{l} CH_3 \\ \\ CH(OH).CH_3 \end{array} \longrightarrow \begin{array}{l} CH_2-CH_2-C-CH_3 \\ |\qquad\qquad\quad \| \\ CH_2-CH_2-C-CH_3 \end{array}$$

The hydrocarbon is also formed by the dehydration of 1.2-dimethylcyclohexanol(1). It is therefore readily prepared from methylcyclohexane-2-one by treating with methyl-magnesium iodide and dehydrating the resulting alcohol. The nitrosochloride is bluish in color, easily volatile with steam and melts at 58°–60°. It yields a dibromide $C_8H_{14}Br_2$ melting at 154°–156° and by oxidation, the glycol melting at 38°–39°.[83]

[81] *Ann.* *360*, 34.
[82] *Ann.* *417*, 255 (1918).
[83] Wallach, *Ann.* *396*, 278 (1913).

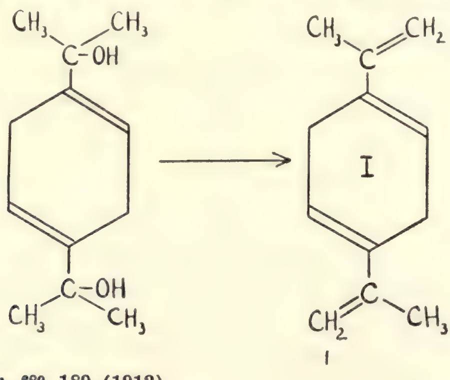
Ethylidenecyclohexane has been synthesized by the Reformatsky synthesis, condensing cyclohexanone and α-bromopropionic acid and decomposing the resulting cyclohexanolpropionic acid

$$
\begin{array}{ccccc}
 & CH_2 - CH_2 & & & \\
/ & & \backslash & & OH \\
CH_2 & & & C< & \\
\backslash & & / & & CH(CH_3).CO_2H. \\
 & CH_2 - CH_2 & & &
\end{array}
$$

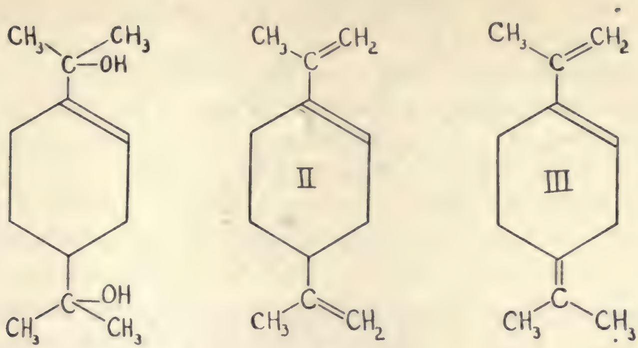
in the usual manner. The nitrosochloride melts at 132°.[83a] Following the general rule that on treating with alcoholic sulfuric acid semicyclic double bond shifts to the ring, ethylidenecyclohexane when so treated yields *ethyl*-Δ^1-cyclohexene. The latter hydrocarbon is more readily prepared by treating cyclohexanone with ethyl-magnesium bromide and dehydrating the resulting tertiary alcohol in the usual manner. Propylidenecyclohexane is similarly prepared and also rearranges readily to propyl-Δ^1-cyclohexene.[84]

The hydrocarbon 1.3-dimethyl-Δ^3-cyclohexene, noted in the above tables, is identical with the so-called "tetrahydro-meta-xylene" obtained by condensing methylheptenone. It yields a nitrosochloride and a characteristic nitrolpiperidide melting at 130°–131°.[85]

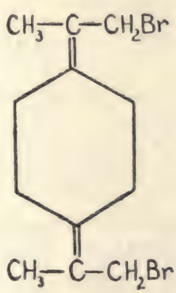
1.4 Di-isopropylcyclohexane: Several unsaturated hydrocarbons having the carbon structure of di-isopropylcyclohexane have recently been prepared by Bogert and Harris[86] by well-known methods of synthesis. When the esters of the hydrogenated terephthalic acids were treated with methyl-magnesium iodide the glycols were not obtained, these passing immediately into the hydrocarbons.



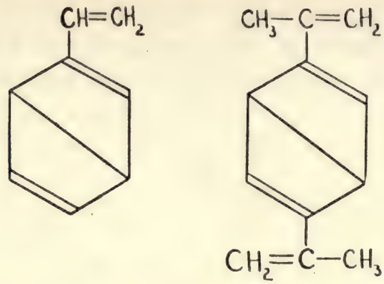
[83a] Wallach, *Ann.* *389,* 189 (1912).
[84] Wallach, *Ann.* *360,* 56.
[85] Wallach, *Ann.* *396,* 264 (1913).
[86] *J. Am. Chem. Soc.* *41,* 1678 (1919).



The hydrocarbon I, 1.4-di-isopropenyl-$\Delta^{1 \cdot 4}$-cyclohexadiene, melts at 117°–117.5°, yields an oily tetrabromide and also a crystalline tetrabromide melting at 107°–109°. When it was attempted to add more bromine, substitution and evolution of hydrobromic acid occurred similar to the behavior of $\Delta^{8 \cdot 8(9)}$-p-menthadiene noted by Perkin, which adds smoothly only two atoms of bromine supposedly on account of the fact that the two double bonds are in the conjugated position. Bogert and Harris regard their liquid and crystalline tetrabromides as *cis* and *trans* isomers of the substance

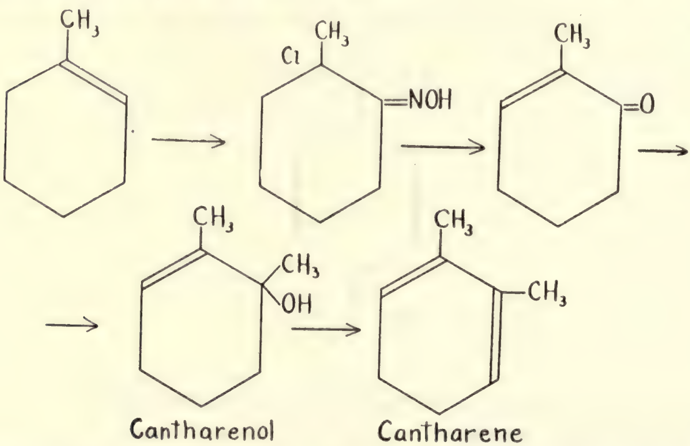


The refractive index of the hydrocarbon was determined in benzene and in chloroform solutions, using Eisenlohr's values, and an exaltation of the molecular refraction, due to the two conjugated double bond systems of 3.776, was found. Bogert and Harris note that almost the same exaltation of the molecular refraction was noted in the case of 1.4-disopropenylbenzene, i.e., 3.841, which they believe points to a structure analogous to Dewar's structure for styrene,



The values obtained for the magnetic rotatory power of p-di-isopropenyl-benzene, however, point to a Kekulé, not a Dewar structure.

Cantharene, a hydrocarbon obtained by the decomposition of cantharidene, has been synthesized by Haworth [87] from 1-methyl-Δ^1-cyclohexene in the following manner. The nitrosochloride of the methylcyclohexene was heated with sodium acetate in acetic acid, removing hydrogen chloride in the usual manner and by hydrolyzing the resulting unsaturated oxime 1-methyl-Δ^6-cyclohexene-2-one was obtained. A methyl group was introduced by means of methylmagnesium iodide and the resulting tertiary alcohol was decomposed by heating with 8 per cent oxalic acid.



Monocyclic Sesquiterpenes: The name "sesquiterpene" has been employed for a number of hydrocarbons of the formula $C_{15}H_{24}$ occurring in essential oils. Semmler has recently made several hydrocarbons of this empirical formula by condensing isoprene with various

[87] *J. Chem. Soc.* **103,** 1242 (1913).

terpenes by heating them together in sealed tubes. Very little is known regarding the constitutions of the sesquiterpenes beyond the fact that some are acyclic and have four double bonds, some are monocyclic and have three double bonds, some are bicyclic having two double bonds and others are tricyclic and have only one double bond. It will readily be understood that the possible number of isomeric hydrocarbons is very great and it now appears that most of the hydrocarbons, described in the literature of twenty years ago as definite hydrocarbons, are in reality mixtures and that the separation of pure individual hydrocarbons from such mixtures is a difficult task indeed. Also it was usually assumed in the literature that the hydrocarbons regenerated from crystalline derivatives, such as the dihydrochlorides, were identical with the original hydrocarbons, whereas many instances are known in which the structure of the regenerated hydrocarbon is quite different from the original.

The monocyclic sesquiterpenes are probably derivatives of cyclohexane and are accordingly so classified. The physical data are often very helpful in showing whether the sesquiterpenes are monocyclic, bicyclic or tricyclic. As noted by Parry [88] the following constants are typical of these several groups.

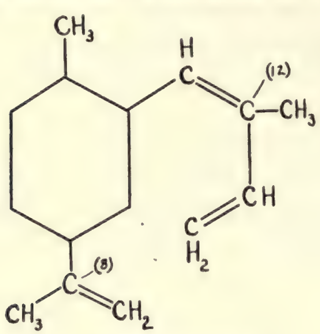
	Specific Gravity	*Mol. Refraction (Calculated)*
Monocyclic sesquiterpenes	0.875 to 0.890	67.76
Bicyclic "	0.900 " 0.920	66.15
Tricyclic "	0.930 " 0.940	64.45

Catalytic hydrogenation by Paal's, Skita's or Willstätter's methods and the reactions with hydrogen chloride or hydrogen bromide also indicate the number of double bonds in the hydrocarbon, hydrogenation being more certain since conjugated linkings frequently do not add the maximum number of molecules of halogen acid.

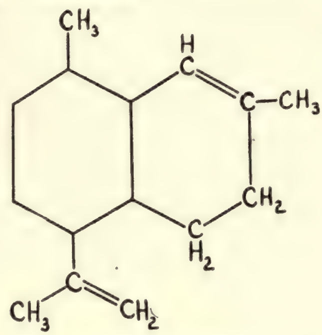
Zingiberene and Zingiberol: This sesquiterpene occurs in ginger oil. According to Semmler and Becker [89] it is monocyclic and contains three double bonds, one of which is in the ring and two in the side chain. The molecular refraction indicates that two of these double bonds are in conjugated positions; MR $= 68.37$, calculated for $C_{15}H_{24}/\overline{}^{3}$ is 67.86. This optical evidence is also supported by its chemical behavior, forming a dihydrochloride, melting at 169°–170°. Catalytic hydrogenation in the presence of platinum gives hexahydro-

[88] "The Chemistry of Essential Oils," Ed. III, Vol. I, 71.
[89] *Ber.* 46, 1914 (1913).

zingiberene $C_{15}H_{30}$, but reduction by sodium and alcohol yields the monocyclic dihydrozingiberene, $C_{15}H_{26}$, which also is good evidence of the existence of two conjugated double bonds, and since this reduction takes place very readily Semmler concludes that these conjugated double bonds are in the side chain. As with other substances containing conjugated double bonds, zingiberene resinifies and polymerizes very readily on standing in the air or warming with sodium. Semmler and Becker state that when zingiberene is treated in acetic acid solution with a little sulfuric acid, that it is condensed to a bicyclic isomer which they have named isozingiberene. They have proposed the following constitution for these two hydrocarbons



Zingiberene



Isozingiberene

Zingiberene forms a nitrosochloride melting at 96°–97° and a nitrosite melting at 97°–98° (by treating zingiberene in cold petroleum ether with acetic acid and sodium nitrite). A nitrosate melting at 86° (with decomposition) is formed by treating the hydrocarbon, dissolved in cold glacial acetic acid, with ethyl nitrite and slowly adding nitric acid.

Zingiberene is associated in the essential oil of ginger, with a sesquiterpene alcohol, zingiberol,[90] which yields zingiberene on decomposition by warming gently with potassium acid sulfate. The alcohol is partially decomposed on treating with acetic anhydride and does not readily yield a phenylurethane, and on treating the alcohol with hydrogen chloride or hydrogen bromide in acetic acid, the dihydrochloride and dihydrobromide respectively, of zingiberene are formed. The alcohol is evidently a tertiary alcohol and from its relations to zingiberene the hydroxyl group must be situated at positions (8) or

[90] Brooks, *J. Am. Chem. Soc.* 38, 430 (1916).

(12) in the above figures. The alcohol has a persistent aroma of ginger oil but does not have the sharp taste of the "gingerol" discovered by Garnett and Greier [91] and recently shown by Nelson,[92] and others [93] to be a phenol derivative. [Cf. particularly Lapworth, Pearson and Royle.] Zingiberol distills at 154°–157° (14.5 mm.).

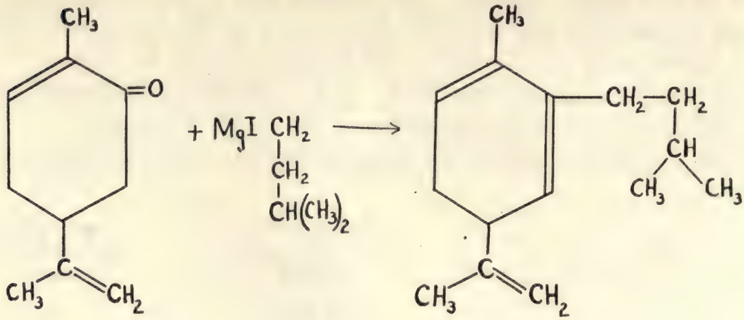
The physical properties of zingiberene, and isozingiberene are as follows,

	Zingiberene	*Iso-zingiberene*
Boiling-point	128°–129° (9 mm.)	118°–122° (7 mm.)
$d_{20°}$	0.8684	0.9118
n_D	1.4956	1.5062
Mol. Ref. calc. for $C_{15}H_{24}/\overline{=}^3$	67.86	....
" " found	68.37	66.50
" " calc. for $C_{15}H_{24}/\overline{=}^2$	....	66.15

According to Semmler and Becker the dihydrochloride noted above is really a derivative of isozingiberene since the latter hydrocarbon is formed from the dihydrochloride by digesting with alcoholic caustic potash. Hydrogenation by platinum black in acetic acid yields hexahydrozingiberene, $C_{15}H_{30}$, boiling-point 128°–129° (11 mm.) $d_{20°}$ 0.8264, n_D 1.4560. Isozingiberene adds only four atoms of hydrogen to form the saturated bicyclic hydrocarbon. Like myrcene and other conjugated dienes, zingiberene is readily condensed by heating at about 215° to a bicyclic isomer, and to a dimeride, $C_{30}H_{48}$, boiling-point 260°–280° (11 mm.), $d_{20°}$ 0.9287.

A synthetic monocyclic sesquiterpene has been made by Roenisch [94] in a manner which leaves little doubt as to its constitution and may properly be named isoamyl-α-dehydrophellandrene. By treating carvone with isoamyl-magnesium iodide (in benzene solution) he obtained the unsaturated hydrocarbon, boiling-point 130°–132° (11 mm.) $d_{22°}$ 0.8679, $[\alpha]_D$ + 18° 30′, n_D 1.49478.

[91] *Chem. Zentr.* *1907*, II, 924; *1909*, II, 1593.
[92] *J. Am. Chem. Soc.* *41*, 1115 (1919); *42*, 597 (1920).
[93] Nomura, *Chem. Abs.* *1917*, 2662; Lapworth, Pearson and Royle, *J. Chem. Soc. III*, 777 (1917).
[94] Schimmel & Co., Semi-Ann. Rep. *1917*, 20.



The synthetic hydrocarbon does not give a solid hydrochloride but is readily hydrogenated by Willstätter's method to the hydrocarbon $C_{15}H_{30}$.

Bisabolene, $C_{15}H_{24}$: This sesquiterpene is monocyclic, contains three double bonds and yields a trihydrochloride $C_{15}H_{27}Cl_3$, melting at 79°–80°. Its constitution is not known but it is probably a derivative of cyclohexane. It was originally discovered in the essential oil of Bisabol myrrh but has since been found in other essential oils, a specimen isolated from lemon oil by Gildemeister and Müller [95] having the following physical properties, boiling-point 110°–112° (4 mm.), $d_{15°}$ 0.8813, $[\alpha]_D$ — 41° 31′, n_D 1.49015. The regenerated hydrocarbons, obtained by heating the trihydrochloride with sodium acetate, distilled at 261°–262°. Bisabolene does not form a crystalline nitrosochloride, nitrosite or nitrosate.

[95] Schimmel & Co., Semi-Ann. Rep. *1909* (2), 50.

Chapter IX. Cyclic Non-benzenoid Hydrocarbons:

The Para-menthane Series.

(1) Limonene and Dipentene.

Limonene occurs in a very large number of essential oils. *Dextro*-limonene is found as the major constituent in the citrus oils, sweet orange peel, lemon, bergamot, lime, mandarin orange and petit-grain oil, also the essential oils of ginger grass, camphor, Manila elemi, caraway and other oils. It is most conveniently isolated from oil of sweet orange peel, constituting about 90 per cent of this oil. *Lævo*-limonene is found chiefly in the leaf oil of the silver fir, turpentine from *Pinus serotina* of the southern United States, one of the species of eucalyptus, *Eucalyptus staigeriana*, American oil of peppermint, oil of verbena, American penny-royal, etc. The optically inactive form, *dipentene*, is also found in nature in the essential oils of lemon grass, palma-rosa, ginger grass, Siberian pine needle, pepper, cubeb, camphor oil, ajowan, coriander, nutmeg, fennel, cardamom, etc. It is also formed by the racemization of *d.* or *l.* limonene by prolonged heating, by the rearrangement of less stable terpenes such as pinene [1] and phellandrene, by the condensation of two molecules of isoprene and is accordingly found in turpentines made by distilling pine stumps and the lighter fractions of rosin or copal oils made by the destructive distillation of rosin or Manila copal and the destructive distillation of caoutchouc. Formerly a number of different names were given to this hydrocarbon, but Wallach [2] showed that the hydrocarbon fractions boiling at 175°–176° from orange peel oil ("hesperidene"), lemon ("citrene"), caraway ("carvene"), bergamot, dill and pine needle oils yielded a tetrabromide melting at 104°, and that the corresponding hydrocarbon variously designated as cinene, cajeputene, kautschin,

[1] On heating pinene with anhydrous oxalic acid a mixture of dipentene and borneol esters are formed, cf. "synthetic camphor."
[2] *Ann.* 227, 277 (1885).

di-isoprene and that from camphor oil, yielded a tetrabromide melting at 125°. On isolating *l.* limonene from pine needle oil Wallach[3] showed that the crystalline tetrabromide appeared to be identical with the tetrabromide from *d*-limonene, except for opposite hemihedral crystal development (like Pasteur's salts of tartaric acid), and that when equal portions of the *d* and *l*-tetrabromides were dissolved and crystallized, the tetrabromide melting at 125° and characteristic of dipentene resulted. This relationship has since been established for other derivatives of limonene and dipentene. It was by such methods that the investigation of the terpenes began to be simplified. Thus the same relation was shown to exist between the nitrolamine derivatives of *d* and *l*-limonene and those of dipentene, or the racemic forms. Wallach[4] discovered that when the nitrosochlorides of *d* or *l*-limonene and dipentene were treated with aniline, condensation to the nitrolanilides resulted, there being six forms. Their relations were made clear by Wallach as indicated in the following diagram,

l-limonene		*d*-limonene	
α-nitrosochloride	β-nitrosochloride	α-nitrosochloride	β-nitrosochloride
↓	↓	↓	↓
α-nitrolanilide M.-P. 113°	β-nitrolanilide M.-P. 153°	α-nitrolanlide M.-P. 113°	β-nitrolanilide M.-P. 153°

racemic, α-dipentene nitrolanilide, M.-P. 126°   racemic, β-dipentene nitrolanilide, M.-P. 149°

Physical Properties: The recorded physical properties of limonene are the following: boiling-point 175°–176°, $d_{15°}$ 0.846 to 0.850, $n_{D}^{20°}$ 1.47459,[5] $[\alpha]_D = +125°\ 36'$,[6] $-105°$, $-119.41°$.[7] A sample of dipentene made by destructive distillation of caoutchouc, examined by

[3] *Ann.* *246*, 221 (1888).
[4] *Ann.* *252*, 94 (1889). For experimental details this paper is recommended.
[5] Wallach, *Ann.* *246*, 222 (1888).
[6] Godlewski & Roshanowitsch, *Chem. zentr.* *1899* (1), 1241.
[7] Gildemeister, *"Aetherische Oele,"* Ed. 2, Vol. I, 325.

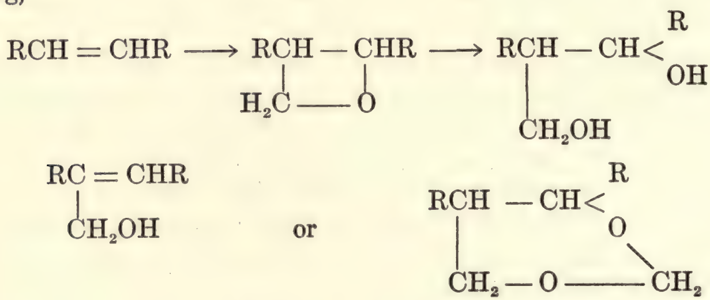
Schimmel and Co.,[7] showed a boiling-point of 175°–176°, $d_{20°}$ 0.844 and $n\frac{20°}{D}$1.47194. The boiling-point of dipentene, 177° to 178°, is usually stated, in the older literature, to be higher than that of limonene but these higher boiling-points (sometimes given as high as 179°) were probably due to the presence of considerable high-boiling terpinene. (Until recently racemic compounds were believed not to persist in the liquid state, but Ladenburg [8] has shown, in the case of pipecoline, that this is possible, and Dunstan and Thole [9] have found, by means of viscosity measurements, evidence that racemic forms may exist in solution.) Limonene shows two broad absorption bands in the ultraviolet spectrum, but the absorption is increased in isomeric *para* menthadienes in which the double bonds are nearer each other; limonene accordingly shows less absorption than other menthadienes.[10] Perkin [11] also showed that limonene has a lower magnetic rotation, $M = 11.24$, than the isomer $\Delta^{3\cdot8(9)}$ menthadiene, $M = 13.06$, the double bonds in the latter hydrocarbon being in the conjugated positions.

Limonene and dipentene are most conveniently identified by means of their tetra-bromides,[12] which are best prepared by adding the calculated amount of bromine to the hydrocarbon dissolved in about four volumes of acetic acid, keeping the mixture chilled during the gradual addition of the bromine. Remarkably high yields of the nitrosochlorides of limonene and pinene can be obtained by following the method recently described by Rupe.[13] Concentrated sulfuric acid and concentrated sodium nitrite solution are separately dropped into a flask containing a thin paste of common salt and concentrated hydrochloric acid. The evolved gases are cooled, dried by passing through calcium chloride and then passed into a solution of limonene in one volume of ether and one half volume of glacial acetic acid, cooled in ice and salt. Heating limonene or dipentene nitrosochlorides with alcoholic caustic alkali yields carvoxime.[14] Both *d* and *l*-carvoxime melt at 72° but the racemic carvoxime, derived from dipentene, melts at 93°. When limonene nitrosochloride reacts with sodium azide the chlorine

[8] *Ber.* *43*, 2374 (1910).
[9] *J. Chem. Soc.* *93*, 1815 (1908); *97*, 1249 (1910). Evidence of racemic menthyl mandelates, cf. Findlay, *J. Chem. Soc.* *91*, 905 (1907).
[10] Hantzsch, *Ber.* *45*, 553 (1912).
[11] *J. Chem. Soc.* *89*, 854 (1906).
[12] Power & Kleber, *Arch. Pharm.* *232*, 646 (1894).
[13] *Helv. chim. Acta.* *4*, 149 (1921).
[14] Deussen & Hahn, *Chem. Zentr.* *1910* (1), 1142.

atom is replaced by the azide group N_3; the resulting nitroso-azide also yields carvoxime on decomposition.[15]

Oxidation of limonene in the presence of water yields carvone, carveol (q.v.) and a resin.[16] Oxidation of limonene by chromyl chloride yields chiefly cymene which is then further oxidized to α-p-tolylpropaldehyde and p-tolylmethyl ketone,[17] resembling terpinene in this respect, but in the case of limonene much more resin is formed. Condensation of limonene with formaldehyde brought about by the use of para-formaldehyde in glacial acetic acid with the addition of a little sulfuric acid, yields an unsaturated alcohol homolimonenol, boiling-point 122°–126° at 13 mm., $d\frac{19^\circ}{4^\circ}$ 0.9720. According to Prins[18] addition of formaldehyde to a double bond occurs to give an oxide ring which may then hydrolyze to a glycol, which in turn decomposes to give an unsaturated alcohol, as in the case of limonene, or many yield a methylene ether, as indicated in the following,



This reaction with formaldehyde has also been studied by Prins in the cases of pinene, camphene, cedrene, etc. When dipentene dihydrochloride, a by-product in the manufacture of artificial camphor, is treated with chlorine to form a trichloromenthane and this product decomposed, cymene is formed.[19]

Carvomenthene: (Δ^1-p-menthene?).

When limonene is hydrogenated in the presence of platinum black, the reduction proceeds in two stages, the first product being carvomenthene and the final product paramenthane.[20] Carvomenthene

[15] Forster & Gelderen, *J. Chem. Soc. 99*, 2061 (1911).
[16] Blumann & Zeitschel, *Ber. 47*, 2623 (1914).
[17] Henderson & Cameron, *J. Chem. Soc. 95*, 972 (1909).
[18] *Chem. Abs. 14*, 1662 (1920).
[19] Brit. Pat. 142,738 (1919).
[20] Vavon, *Bull. Soc. chim.* (4) *15*, 282 (1914).

made in this manner is optically active, $[\alpha]_{578}$ $+118°$. Bacon [21] prepared carvomenthene from limonene monohydrochloride (by HCl in cold carbon bisulfide solution) by making the Grignard complex, magnesium limonene hydrochloride, and decomposing this with water. However, racemization accompanies the formation of the hydrochloride. Bacon also made the hydrochloride of carvomenthene and reduced it to para-menthane in the same manner by means of the Grignard reaction. Carvomenthene boils at 175°–177°, its hydrochloride boils at 85°–86° (13 mm.) and the nitrosochloride melts at 95°.

Para-menthane: By the catalytic reduction of limonene by hydrogen in the presence of platinum black,[22] by the hydrogenation of para-cymene in the presence of catalytic nickel [23] and by heating the semicarbazone or hydrazone [24] of menthone with sodium ethylate at 160°–170°, para-menthane is produced, boiling-point 169°, d $\frac{15°}{15°}$ 0.803. In the latter process heating the semicarbazone at 160° first forms the hydrazone which subsequently decomposes to the hydrocarbon,

$$>C = N.NH.CONH_2 + H_2O \longrightarrow >C = N.NH_2 + CO_2 + NH_3$$

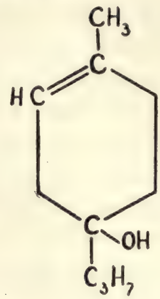
The Constitution of Limonene: The structure of limonene is intimately related to the structure of terpineol, terpin and carvone. Tilden [25] and Wallach [26] had, at an early date, shown that when terpin is digested with dilute acids, it yields terpineol and that by more energetic dehydration terpineol also decomposes further, forming water and dipentene.

$$\underset{\text{terpin}}{C_{10}H_{18}(OH)_2} \longrightarrow \underset{\text{terpineol}}{C_{10}H_{17}.OH} \longrightarrow \underset{\text{dipentene.}}{C_{10}H_{16}}$$

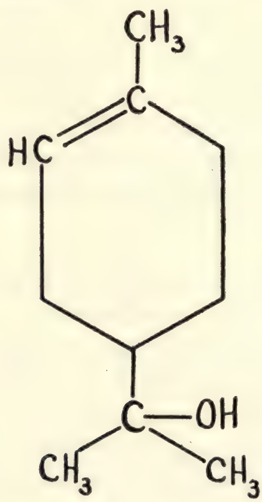
Terpineol and terpin are converted by hydrogen chloride to a crystalline dichloride [27] $C_{10}H_{18}Cl_2$ melting at 50°, which is identical with the dihydrochloride made from dipentene.[26] The position of the double bond in terpineol was suggested by Wallach [28] and confirmed by later researches of Baeyer [29] and others, particularly on the ground of the

[21] *Philippine J. Sci. 1908,* 52.
[22] Vavon, *Compt. rend. 149,* 997 (1909).
[23] Sabatier & Senderens, *Compt. rend. 156,* 184 (1913).
[24] Wolff, *Ann. 394,* 86 (1912).
[25] *Ber. 12,* 848 (1879) ; *J. Chem. Soc. 35,* 287 (1879).
[26] *Ann. 230,* 258 (1885).
[27] List, *Ann. 67,* 367 (1848).
[28] *Ann. 277,* 105 (1893).
[29] *Ber. 26,* 2558 (1893).

relations between terpineol and carvone (see below). Wallach's proposed constitution of terpineol was



This proposed structure was open to the objection that such a substance could not decompose with loss of water to give a hydrocarbon containing an asymmetric carbon atom, whereas Wallach himself had shown that dipentene was a mixture of the two active *d* and *l*-limonenes. A little later, 1894, Wagner[30] published his well-known paper "On the oxidation of cyclic compounds," in which he modified Wallach's terpineol structure to



which is abundantly supported by other evidence published since, of which probably the most convincing is W. H. Perkin, Jr.'s synthesis of terpin, terpineol and a series of related substances.[31]

[30] *Ber.* 27, 1636 (1894).
[31] 8th *Int. Cong. Appl. Chem.* VI, 224 (1912).

The group $R-\overset{CH_3}{\underset{CH_3}{C}}-OH$ is readily synthesized by the action of zinc methyl, and particularly easily by the action of magnesium methyl iodide on acid chlorides, esters or methyl ketones and Perkin accordingly carried out his synthesis as follows:

(1) Pentane-1, 3, 5-tricarboxylic acid was heated with acetic anhydride when CO_2 and water were eliminated and cyclohexanone-4-carboxylic acid was formed.

$$\begin{matrix} HO_2C.CH_2CH_2 \\ HO_2C.CH_2CH_2 \end{matrix}\!>CH.CO_2H \longrightarrow OC\!<\!\begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix}\!>CH.CO_2H$$

(2) The ester of this acid was then treated with methyl-magnesium iodide in the usual manner when the ketone group reacts much more readily than the CO_2R group; the resulting hydroxy acid was converted to the corresponding bromide by heating with hydrobromic acid and the resulting tertiary bromide digested with sodium carbonate, removing HBr to give 1-methyl-Δ^1-cyclohexene-4-carboxylic acid.

$$OC\!<\!\begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix}\!>CH.CO_2R \longrightarrow \begin{matrix} HO \\ CH_3 \end{matrix}\!>C\!<\!\begin{matrix} CH_2CH_2 \\ CH_2CH_2 \end{matrix}\!>CH.CO_2R$$

$$\rightarrow \begin{matrix} Br \\ CH_3 \end{matrix}\!>C\!<\!\begin{matrix} CH_2CH_2\diagdown \\ CH_2CH_2\diagup \end{matrix}CH.CO_2H \rightarrow CH_3-C\begin{matrix} /\!\!/CH.CH_2 \\ \diagdown CH_2CH_2 \end{matrix}\!>CH.CO_2H$$

(3) On treating the ester of this acid with methyl-magnesium iodide an almost quantitative yield of *α-terpineol* was obtained.

$$CH_3C\begin{matrix} /\!\!/CHCH_2\diagdown \\ \diagdown CH_2CH_2\diagup \end{matrix}CH.CO_2R \rightarrow CH_3C\begin{matrix} /\!\!/CHCH_2\diagdown \\ \diagdown CH_2CH_2\diagup \end{matrix}CH-\overset{CH_3}{\underset{CH_3}{C}}-OH$$

α-Terpineol is characterized by its fine odor of lilacs and is manufactured in comparatively large quantities by decomposing terpin hydrate or terpin (made from pinene) by means of phosphoric acid. Unless specially purified the commercial product is liquid at ordinary temperatures and contains a little β-terpineol [32] melting when pure at

[32] Stephan & Helle, *Ber.* 35, 2147 (1902).

32°, and the liquid terpinenol-1.[33] In nature, only α-terpineol appears to be formed. Terpineol is the major constituent of commercial long leaf pine oil [34] made by distilling the wood with steam. A good commercial pine oil will show 75 per cent distilling between 211° and 218°. It has proven particularly valuable for the concentration of low-grade copper ores by the flotation process. The stability of terpineol in the presence of alkali renders it valuable in the perfuming of soaps. Commercial α-terpineol melts at 35°, boils at 217°–218° at 760 mm., at 104°–105° and 10 mm., has a density of 0.935 to 0.940 at 15° and a refractive index $n\frac{20°}{D}$ 1.4808.[35] An exceptionally pure specimen of α-terpineol, made by Wallach [36] by the action of dilute sulfuric acid on homonopinol, showed melting-point 37°–38°, boiling-point 218°–219°, and $[\alpha]_D - 106°$ (in 16.34 per cent solution in ether). The highest optical activity observed for natural terpineol is $[\alpha]_D + 95° 9'$ (from bitter orange peel oil) and $[\alpha]_D - 27° 20'$ shown by a specimen of *l*-terpineol from linaloe oil. A specimen of synthetic *l*-terpineol [37] showed $[\alpha]_D - 117.5°$. Commercial terpineol is soluble in 9 volumes of 50 per cent, in 3 volumes of 60 per cent and in about 2 volumes of 70 per cent alcohol. When free from water it is miscible in petroleum ether. The nitrosochloride of *d* or *l*-terpineol melts at 107°–108°, that of *i*-terpineol at 112°–113°; the corresponding nitrolpiperidine compounds melt at 151°–152° and 159°–160° respectively. By shaking terpineol with an excess of concentrated hydriodic acid the dihydroiodide $C_{10}H_{18}I_2$ is formed, melting at 77°–78°. Terpineol, being a tertiary alcohol, is very easily decomposed with loss of water when heated with potassium acid sulfate or oxalic acid; even acetic anhydride partially decomposes it, on heating, forming dipentene. Phenylisocyanate yields a phenylurethane,[38] the inactive form melting at 113°. The α-naphthylurethane [39] melts at 147°–148°. As with most tertiary alcohols, the phenyl and naphthylurethanes are difficult to prepare, partial decomposition of the alcohol, with the formation of water, causing the conversion of phenyl isocyanate to diphenyl urea. In preparing the isocyanate it is advisable to separate the crystals of

[33] Wallach, *Ann.* *362*, 269 (1908).
[34] Teeple, *J. Am. Chem. Soc.* *30*, 412 (1908); *Met. & Chem. Eng.* *11*, 247 (1913).
[35] Gildemeister, *"Aetherische Oele,"* Ed. 2, Vol. I, 394.
[36] *Ann.* *360*, 89 (1908).
[37] Ertschikowsky, *Bull. soc. chim.* (3) *16*, 1584 (1896).
[38] Wallach, *Ann.* *275*, 104 (1893).
[39] Schimmel & Co. Semi-Ann. Rep. 1906 (2), 33.

diphenyl urea, which first form, by taking up the liquid portion in a little perfectly dry ether. The mixture should be permitted to stand three or four days protected from the moisture of the air. Good yields of terpinyl hydrogen phthalate and succinate can be obtained by allowing an excess of the alcohol to stand with the acid anhydride at temperatures below 100°.[40] The d-glucosides of both α and β-terpineol have been made by treating β-tetra-acetylbromoglucose in ethyl ether with an excess of the terpene alcohol in the presence of silver carbonate. The acetyl groups are removed from the product by means of barium hydroxide. The resulting glucosides are rapidly hydrolyzed by hot dilute acids but are very slowly split by emulsin.[41] Glucosides of citronellol and of dihydrocarveol were prepared in the same manner. It is practically certain that glucosides of many terpene alcohols exist in nature, in addition to the few, such as coniferin, which are known to occur in nature.

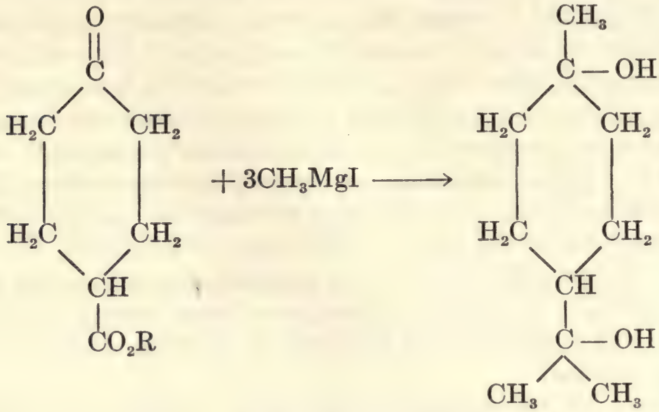
Tertiary alcohols appear to be capable of forming addition products with chromic acid, when the alcohols are dissolved in an inert solvent and shaken with concentrated chromic acid or the solid crystals. In the case of α and β-terpineols the addition products are liquid and unstable.[42]

The hydration of α-terpineol to terpin hydrate can be beautifully demonstrated, as for a lecture experiment, by dissolving terpineol in 5 parts of 80 per cent phosphoric acid at 30°, allowing to stand a few minutes and then diluting about six times with cold water, when within a few minutes a bulky matted mass of crystals of terpin hydrate will form.[43] The reaction is less complete with 60 per cent sulfuric acid and Aschan [44] has shown that 45 per cent sulfuric acid, shaken with pinene for 16 hours at + 1° gives a yield of 53 per cent terpin. The ease of making terpin hydrate from commercial long leaf pine oil has been pointed out by Teeple.[45]

The synthetic α-terpineol made by Perkin was converted into terpin hydrate by agitating with dilute sulfuric acid; by heating with potassium hydrogen sulfate dipentene was obtained, thus completing the synthesis of these three important substances. Additional proof of the constitution of terpin was furnished by Perkin and Kay, who showed

[40] Pickard, Lewcock & Yates, *Proc. chem. Soc.* **29**, 127 (1914).
[41] Haemaelaeinen, *Biochem. Z.* **49**, 398 (1913).
[42] Wienhaus, *Ber.* **47**, 322 (1914).
[43] Prins, *Chem. Abs.* **1917**, 2773.
[44] *Chem. Abs.* **1919**, 2759.
[45] *Loc. cit.*

that when ethyl cyclohexanone-4-carboxylate was treated with large excess of methyl-magnesium iodide, terpin is formed.



1.8-*terpin.*

This synthesis proves conclusively the position of the two hydroxyl groups in terpin.

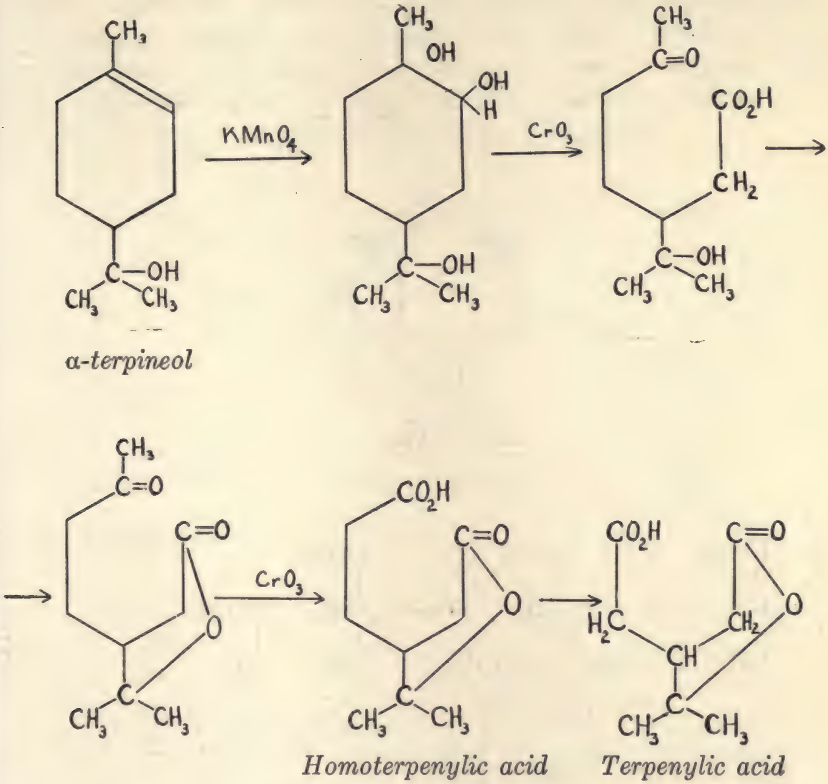
Terpin Hydrate is not known to occur in essential oils. It melts at 116°–117° and readily loses a molecule of water on heating or on standing over sulfuric acid to form terpin, melting-point 104°, whose structure is shown above. Terpin exists in two stereo-isomeric forms of the *cis* and *trans* type.[46] Terpin derived from terpin hydrate by dehydration is the *cis* form; the *trans* form, melting-point 156°–158°, is made from *trans*-dipentene dihydrobromide and silver acetate. *Trans*-terpin does not crystallize with water of crystallization.

Other evidence for the structure of limonene, α-terpineol and terpin had already shown their constitution with reasonable certainty. Wagner had proposed his now accepted constitution of α-terpineol largely to overcome the objection made against Wallach's constitution, that the latter could not give an optically active hydrocarbon, limonine, on dehydration. By oxidizing α-terpineol first with permanganate and then with chromic acid, Wallach[47] obtained a series of oxidation products finally resulting in homoterpenylic and terpenylic

[46] Baeyer, *Ber.* 26, 2865 (1893) ; 29, 5 (1896). Van't Hoff, in 1874, had predicted that cyclic compounds of this type would be found to exist in two stereo isomeric forms.

[47] *Ann.* 227, 110 (1893).

acid and he showed that these changes could readily be interpreted by Wagner's constitution for α-terpineol, i.e.,

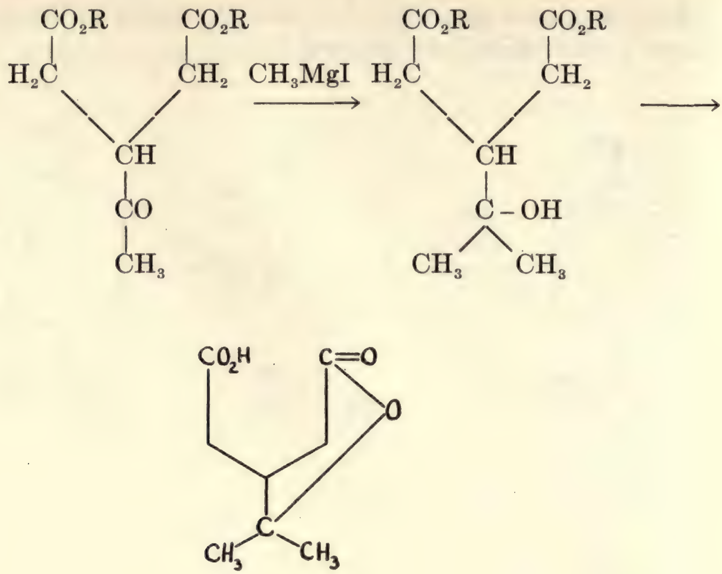


Although the constitution of these important acids was worked out with reasonable certainty [48] their synthesis by Lawrence and Simonsen [49] removes all question as to their structure. The constitution of these acids also has a very direct bearing on the constitution of pinene and Simonsen's synthesis is therefore mentioned in outline as follows,

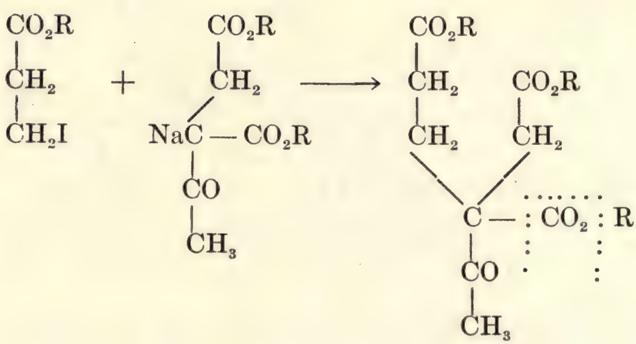
[48] Wallach (*Ann.* *259,* 322 [1890]), had suggested the above constitution for terpenylic acid and its correctness has been confirmed by the work of Fittig (*Ann.* *288,* 176 [1896]), Mahla and Tiemann (*Ber.* *29,* 928 [1896]), and Schryver (*J. Chem. Soc.* *63,* 1338 [1893]).

[49] *J. Chem. Soc.* *75,* 527 (1899); *91,* 184 (1907).

(a)



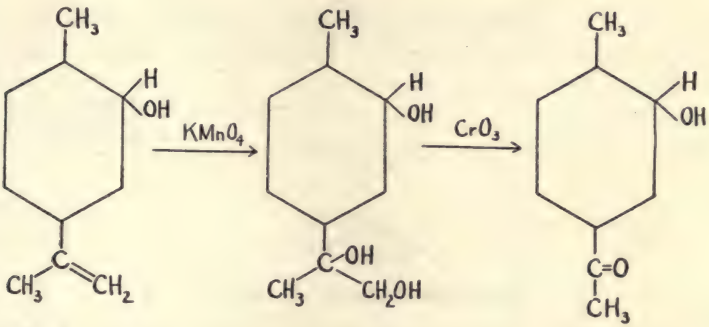
(b)



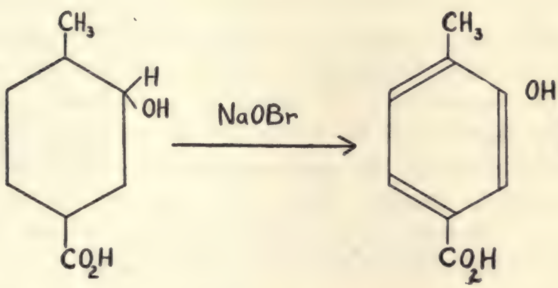
When the latter ester is hydrolyzed with hydrochloric acid, CO_2 is eliminated; the ester of the resulting β-acetyladipic acid yields homoterpenylic acid (ester) when treated with magnesium-methyl iodide, as in (a).

The above work, together with Perkin's synthesis, conclusively proves the position of the double bond in α-terpineol. The position of the other double bond in limonene was shown by reference to the constitution of carvone and dihydrocarveol. The nitrosolimonene of

Tilden and Shenstone[50] proved to be identical with carvoxime,[51] from which it follows that at least one and perhaps both double bonds in limonene and in carvone are similarly situated. On reduction of carvone one double bond is saturated yielding dihydrocarveol, which on oxidation first by permanganate, followed by chromic acid and sodium hypobromite, finally yields 2-hydroxy-*para*-toluic acid, which, when the intermediate products are also considered, indicates that the double bond in dihydrocarveol is in the side chain.[52]



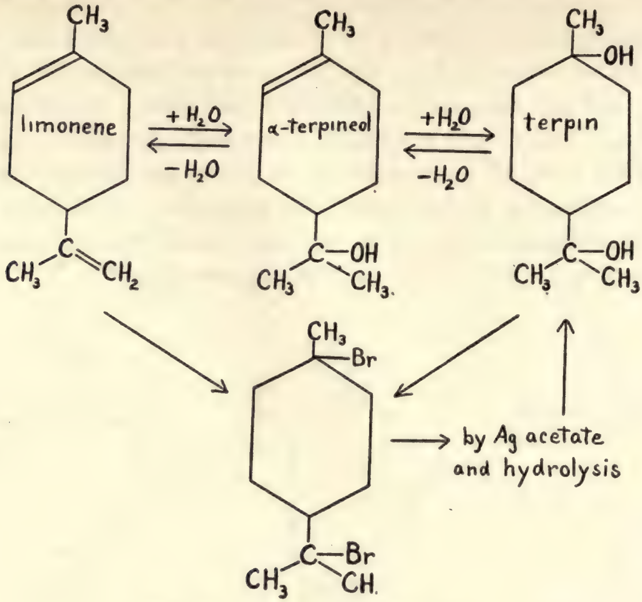
Dihydrocarveol



2-hydroxy-para-toluic acid

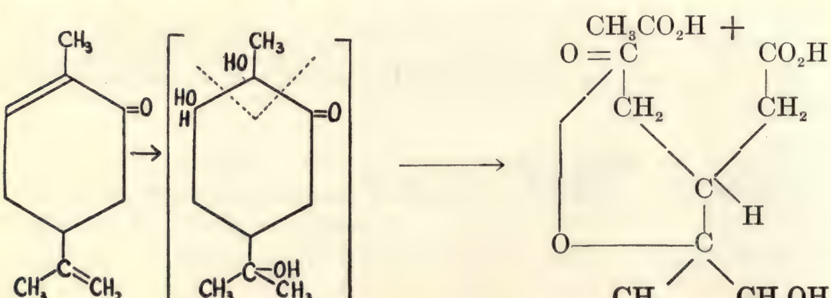
The above facts make clear the relations between limonene, α-terpineol and terpin, and the dihydrohalogen derivatives obtained from all three, i.e.,

[50] *J. Chem. Soc. 31*, 554 (1877).
[51] Goldschmidt & Zürrer, *Ber. 18*, 2220 (1885).
[52] Wallach, *Ann. 275*, 110 (1893); Tiemann & Semmler, *Ber. 28*, 2141 (1895).

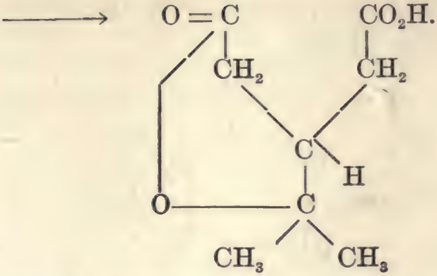


The Constitution of Carvone.

The conversion of carvone to carvacrol, and carvoxime to carvacrylamine were early observed and, though not understood, served to call attention to the probability that carvone, carvoxime and limonene were para-menthane (1-methyl-4-iso propylcyclohexane) derivatives and that the oxygen atom in carvone occupied position (2). Wagner [53] with his usual perspicacity, proposed a constitution for carvone in 1894, which has proven correct. He based his deductions upon the results obtained by Best [54] and by Wallach [55] on oxidizing carvone, although the constitutions of the oxidation products they obtained were not then definitely known. Terpenylic acid can be obtained from carvone in the following manner, the ring being broken at two points to give acetic acid as one of the oxidation products.

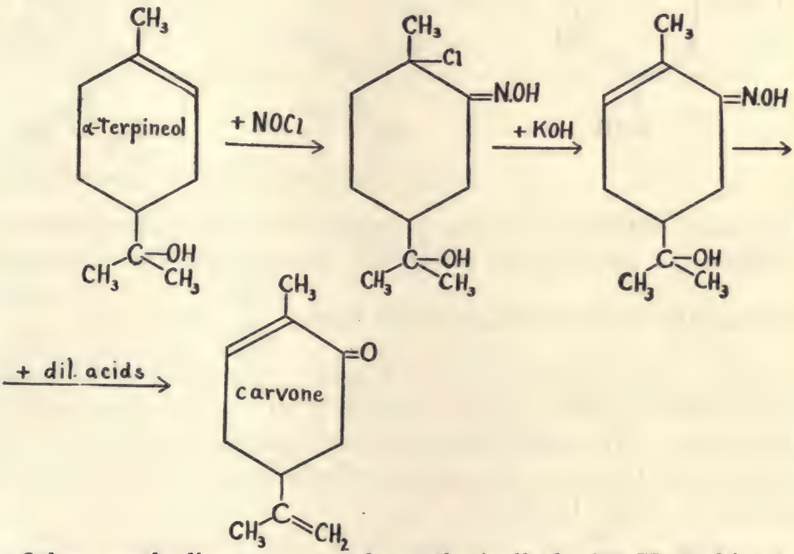


[53] *Ber.* 27, 2270 (1894). [54] *Ber.* 27, 1218 (1894). [55] *Ber.* 27, 1496 (1894).



(by replacing OH by Br and reducing)

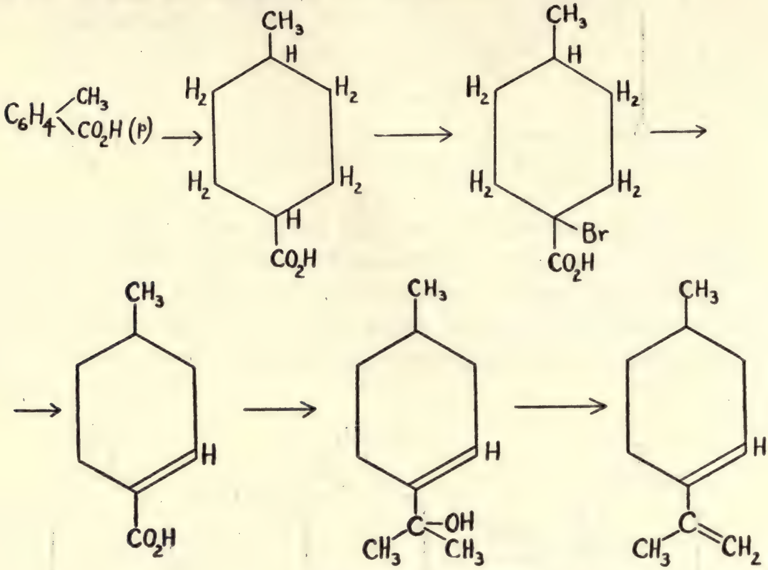
The relation between carvone and limonene is very well shown by Wallach's[56] conversion of terpineol to carvone by removing hydrogen chloride from terpineol nitrosochloride by means of caustic alkali and then boiling the resulting oxime with acids, thus hydrolyzing the oxime to the ketone and simultaneously removing the original hydroxyl group.



Other menthadienes were made synthetically by W. H. Perkin, Jr., and his assistants. $\Delta^{3 \cdot 8(9)}$-p-menthadiene was made in the following manner. *Para*-toluic acid was reduced by sodium and alcohol to 1-methylcyclohexane-4-carboxylic acid which on bromination, followed by removal of HBr by sodium carbonate or quinoline in the usual manner, yielded 1-methyl-Δ^3-cyclohexene-4-carboxylic acid the ester of which yields Δ^3-p-menthenol(8) when treated with mag-

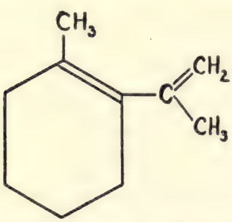
[56] *Ann.* 277, 120 (1893).

nesium methyl iodide. On digesting this menthenol with potassium acid sulfate $\Delta^{3\cdot8(9)}$-p-menthadiene is formed.

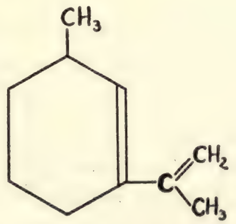


Δ^{3}-p-menthenol(8) *$\Delta^{3.8(9)}$-p-menthadiene*

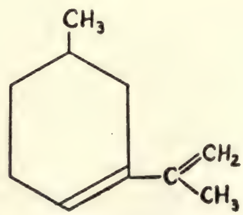
Like many substances having two double linkings in the conjugated position, this menthadiene reacts with bromine to form a dibromide in which the double bond has shifted to the $\begin{matrix} CHBr \\ CH_2 \end{matrix} > C = C < \begin{matrix} CH_2Br \\ CH_3 \end{matrix}$ position. Also, as contrasted with limonene, this menthadiene is capable of combining with only *one* molecule of HCl or HBr, these products being liquid. The same behavior toward bromine and HBr and HCl is shown by the *ortho* and *meta*-menthadiene derivatives containing conjugated double bonds, i.e.,



$\Delta^{1.8(9)}$-o-menthadiene

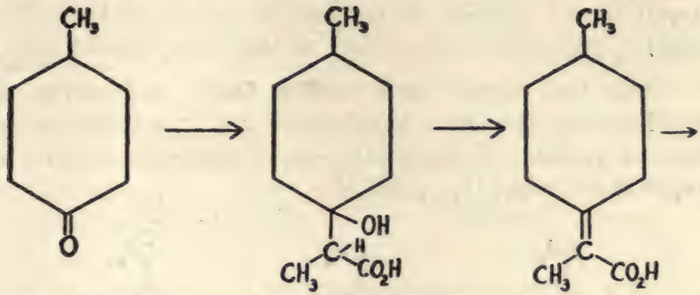


$\Delta^{2.8(9)}$-m-menthadiene

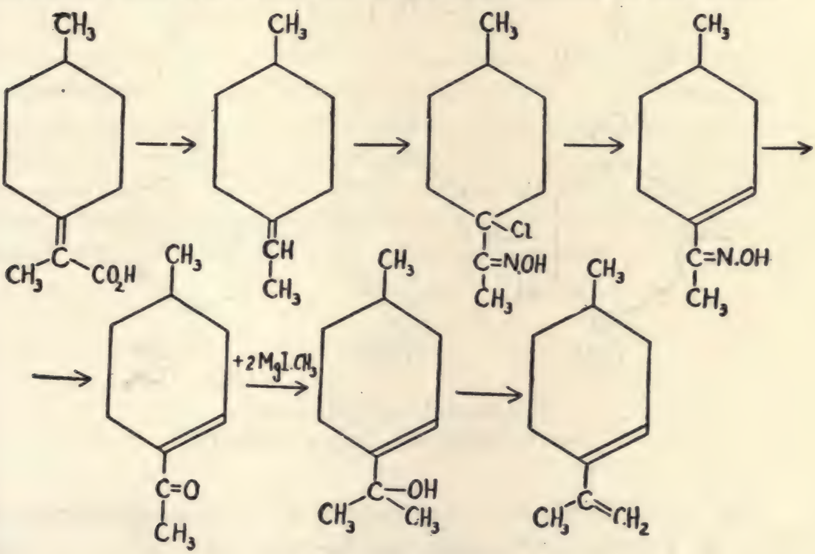


$\Delta^{3.8(9)}$-m-menthadiene

Another synthesis of $\Delta^{3 \cdot 8(9)}$-p-menthadiene was developed by Perkin in collaboration with Wallach.[57] In this synthesis 1-methylcyclohexane-4-one is condensed, by the Reformatsky reaction (zinc and α-bromopropionic ester), to the oxy acid.



The oxy acid loses water, when digested with acetic anhydride, and the resulting unsaturated acid decomposes further when distilled, losing CO_2. The semicyclic hydrocarbon was then converted into its nitrosochloride and this by eliminating hydrogen chloride by alkali yields an oxime which was hydrolyzed in the usual manner to the ketone.



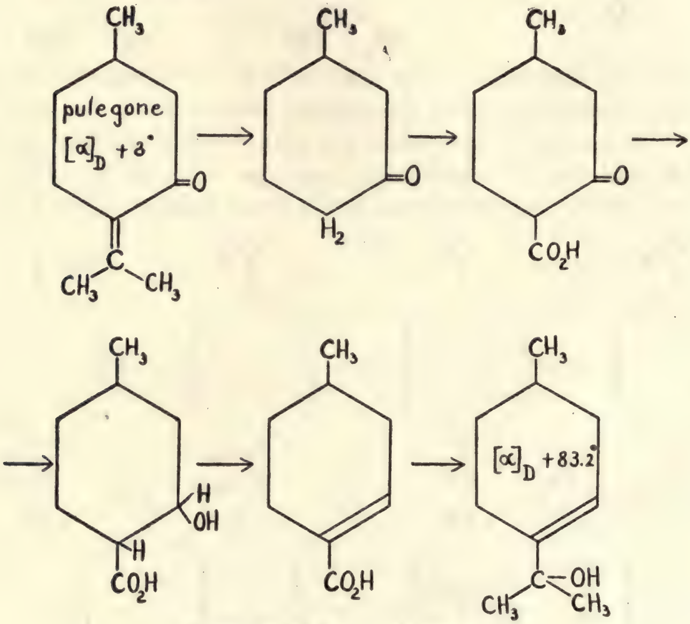
Δ^3-p-menthenol(8)

The ease with which this teriary alcohol is decomposed with loss of water to form the $\Delta^{3 \cdot 8(9)}$-p-menthadiene is worthy of note; shaking

[57] *Ann.* 374, 198 (1910).

with 1 per cent sulfuric acid at warm temperature effects this change.

The products obtained by these methods are, of course, optically inactive and therefore, to obtain Δ^3-p-menthenol(8) of high optical activity, Perkin selected natural pulegone as his original material. As is well known, pulegone decomposes on heating with alkali to give 1-methyl-cyclohexane-3-one, which in this case showed $[\alpha]_D + 8°$. By treating this ketone with sodium amide and carbon dioxide 1-methyl-cyclohexane-3-one-4-carboxylic acid was formed which was dehydrated yielding *d* 1-methyl-Δ^3-cyclohexene-4-carboxylic acid of high optical activity $[\alpha]_D + 150.1°$



l-methyl-Δ³-cyclohexene-4-
-carboxylic acid, $[\alpha]_D + 150.1°$

The following physical properties of $\Delta^{3,8(9)}$-p-menthadiene were noted by Perkin and Wallach: boiling-point 184°–185°, d — 0.858, $n\frac{20°}{D}$ 1.4924 from which the molecular refractivity is 46.02, calculated for $C_{10}H_{16}/=^2$ is 45.24 showing the exaltation due to the conjugated position of the double bonds.

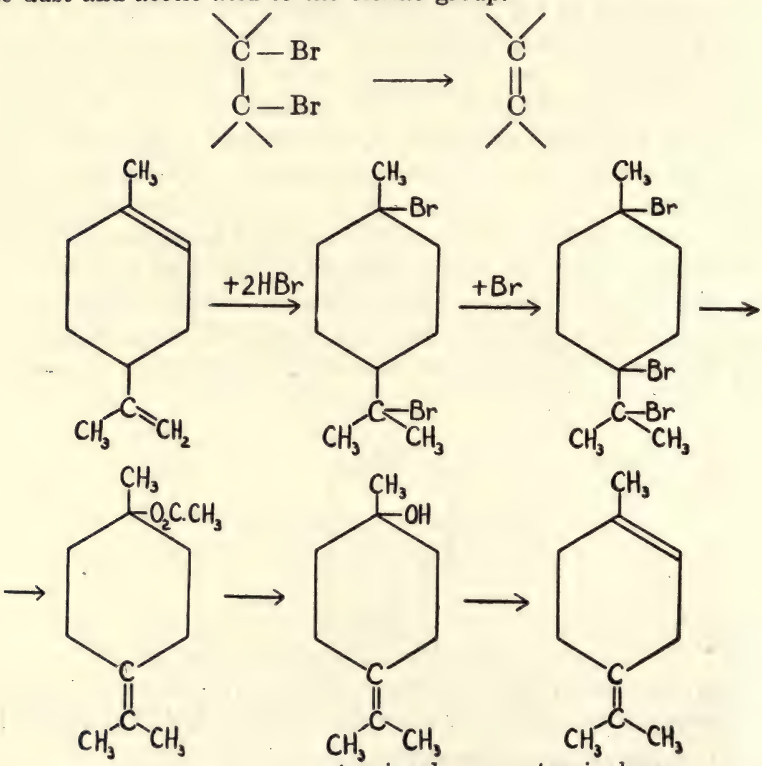
Terpinolene and the Terpinenes.

The constitution of the terpinenes has been a matter of considerable controversy but researches of recent years, particularly the work of Wallach, has solved the puzzle in a very satisfactory manner. Tilden, Armstrong and others had studied the action of mineral acids on turpentine or pinene, also limonene and the alcohols, terpineol and terpin, but the chief result of their investigations was to the effect that a new terpene, $C_{10}H_{16}$, was probably formed. It was not definitely characterized either by physical constants or chemical derivatives, and it was given a variety of names. In 1885 Wallach [58] applied his tetrabromide method, which he had used in the identification of limonene and dipentene, to the high-boiling fraction boiling from 179°–190°, obtained by the action of alcoholic sulfuric acid on turpentine. From this fraction he prepared a new tetrabromide, $C_{10}H_{16}Br_4$ melting at 116°–117°, thus proving the existence of a new terpene, which he named "terpinolene." In the mixture of hydrocarbons resulting from the action of alcoholic sulfuric acid on terpin hydrate, dipentene, phellandrene or cineol, he showed that the fraction boiling from 179°–182° contained what he termed "terpinene." This fraction did *not* give a crystalline tetrabromide. A fairly good yield of terpinolene was also obtained by the action of hot concentrated oxalic or formic acid on α-terpineol, the terpineol being slowly dropped into the acid and the terpinolene removed by distilling with steam as fast as formed, as otherwise the new terpene underwent further change. Being influenced by the constitution for α-terpineol which he had proposed, Wallach [59] suggested the following structure for terpinolene,

Although von Baeyer had accepted Wallach's α-terpineol formula, he nevertheless advanced his now generally accepted $\Delta^{1,4(8)}$ structure for

[58] *Ann.* *227*, 283 (1885); *230*, 262 (1885).
[59] *Ann.* *227*, 145 (1893). This formula was later put forward by Harries, *Ber.* *35*, 1169, as the constitution of terpinene (q.v.).

terpinolene. Baeyer [60] considered that this structure was indicated by the formation of blue nitroso derivatives. The position of the second double bond was indicated by its relation to α-terpineol and its optical inactivity. In view of the fact that other isomeric hydrocarbons are also simultaneously formed and that radical changes in constitution are known to be brought about by heating with acids, these considerations would have little weight were it not for other evidence. Baeyer made terpinolene by brominating limonene dihydrobromide and treating the resulting tribromide with zinc dust; saponification of the resulting mono-acetate yielded a new terpineol, γ-terpineol, melting-point 69°–70°. Baeyer had shown that other substances containing the group $>C=C(CH_3)_2$, for example, tetramethylethylene, give blue nitroso compounds. He had also shown that generally dibromides in which the two bromine atoms are in the 1.2 position are reduced by zinc dust and acetic acid to the olefine group.



γ-terpineol
M.-P. 69°–70°

terpinolene

[60] *Ber.* 27, 436 (1894).

Also since the nitrosochloride of γ-terpineol was also blue, Baeyer reasoned that this terpineol contained the $>C = C(CH_3)_2$ group as in terpinolene. Dehydrating agents were shown to convert γ-terpineol to terpinolene.

Semmler[61] has made a terpinolene of unusual purity by reducing terpinolene tetrabromide (which can be isolated from impure material) by treating with zinc dust in alcohol instead of acetic acid. Semmler's terpinolene had the following physical properties: Sp. Gr. 20°, 0.854, $n \frac{20°}{D}$ 1.484, boiling point at 10 mm. 67°–68°, boiling-point at 760 mm. 183°–185°, optically inactive. Heat converts terpinolene to dipentene and acids partially convert it to a mixture containing α and γ-terpinenes, dipentene and terpinolene. Terpinolene is apparently not found in nature; Clover[62] reported it in Manila elemi, but Bacon,[63] working on material from the same source, was unable to confirm this. Terpinolene is obtained as a by-product in the manufacture of commercial terpineol and is occasionally found as an adulterant of lavender and other oils. Terpinolene has been synthesized from nopinone and methyl nopinol (q.v.).[64]

The Terpinenes.

The formation of "terpinene" by the action of alcoholic sulfuric acid on pinene, terpin hydrate, cineol, dipentene and phellandrene has been mentioned in connection with terpinolene, which is also formed in the reaction mixture. Its occurrence in nature was first noted in the case of oil of cardamoms by Weber.[65] It has been reported to occur in Manila elemi, but according to the researches of Clover and Bacon,[66] on over a hundred specimens of authentic material, different individual trees yield an oleoresin containing either limonene or phellandrene of remarkable purity; the commercial oil accordingly contains both of these terpenes, but since Clover and Bacon worked with fresh material it is probable that the terpinene reported by others was formed from phellandrene by the action of formic or other acids developed by air oxidation. "Terpinene" has usually been identified by means of the nitrosite melting at 155°. According to Schimmel

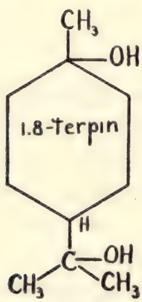
[61] *Ber.* *42*, 4644 (1909).
[62] *Philippine J. Sci.* *1907*, 1.
[63] *Philippine J. Sci.* A. *1909*, 93.
[64] Wallach, *Ann.* *356*, 244 (1907).
[65] *Ann.* *238*, 107 (1887).
[66] *Philippine J. Sci.* *1909*, 93.

& Co.,[67] Wallach's α-terpinene occurs in coriander oil and γ-terpinene in ajowan, lemon and coriander oil.

Terpinene was frequently confounded with dipentene, in the earlier literature. Both yield crystalline addition products with halogen acids, but although the melting points of the corresponding dihydrohalides are very close together, a marked lowering of the melting-point results when the two are mixed. The terpinene dihydrohalides are best prepared from sabinene.

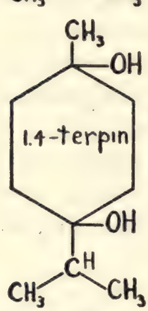
	"Terpinene"	*Dipentene*
$C_{10}H_{16}.2HCl$	51°–52°	50°
$C_{10}H_{16}.2HBr$	58°–59°	64°
$C_{10}H_{16}.2HI$	76°	77°

Wallach[68] has shown that with aqueous alkali the dihydrochloride is converted into a terpin melting at 137° and not identical with *cis* or *trans*-1.8-terpin which corresponds to limonene dihydrochloride. Wallach reasoned that if the new terpin was a di-tertiary alcohol, as its behavior indicated, it must have the structure of 1.4-dihydroxy-p-menthane, if it was in fact a para-menthane derivative. It was further distinguished from ordinary or 1.8-terpin by the formation of an oxide differing from cineol (eucalyptol). It should be men-



M.-P. *cis*- 102°–105° $-H_2O$ ⟶ 1.8 *cineol*

trans- 156°–158°



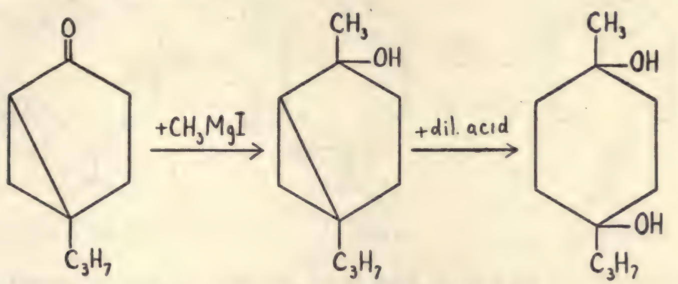
M.-P. *cis*- 116°–117° $-H_2O$ ⟶ 1.4 *cineol*

trans- 137°

[67] Gildemeister & Müller, *Wallach-Festschrift 1909*, 443.
[68] *Ann.* *350*, 157 (1906); *356*, 200 (1907).

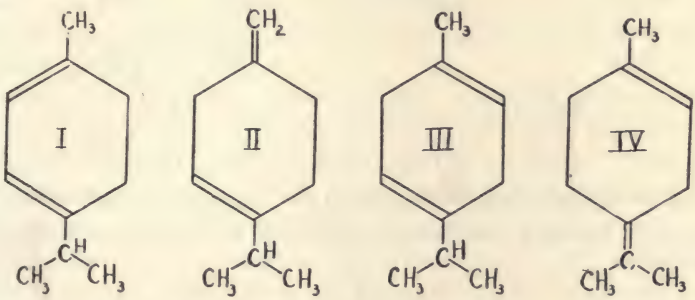
tioned that on dehydrating ordinary terpin, one of the products is the oxide, cineol, which has been shown to be an oxygen ether, or oxide, the oxygen atom of which is attached to the carbon atoms 1 and 8. The difference between the two terpins and their oxides are, as suggested by Wallach.

Additional evidence that this is the constitution of the new terpin was furnished by its synthesis[69] from sabina ketone. (Sabinene and sabina ketone, q.v., had already been shown to contain an unstable tri-carbon ring, as shown.)



Reduction of ascaridol (q.v.) also yields 1.4-terpin.

It will be evident that 1.4-terpin, or the corresponding dihydrochloride, can conceivably decompose with loss of two molecules of water or hydrochloric acid, respectively, to give four different *para*-menthadienes, i.e.,



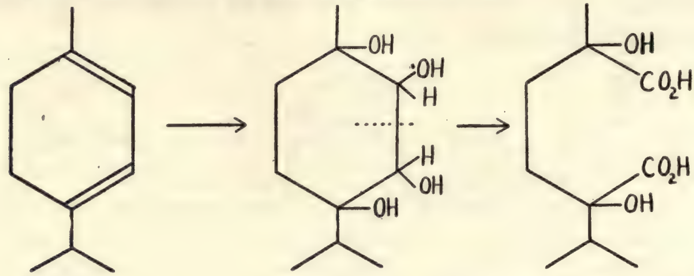
α-*terpinene* β-*terpinene* γ-*terpinene* *terpinolene*

Of the hydrocarbons represented above IV has the constitution which had already been shown to be that of terpinolene. A hydrocarbon having the structure represented by II, $\Delta^{3 \cdot 1(7)}$-p-menthadiene, has been synthesized by Wallach[70] from sabina ketone and found to yield a tetrabromide melting at 154°–155°, and boiling at 173°–174°. It is

[69] Wallach, *Ann.* *357*, 64 (1907).
[70] *Ann.* *357*, 68 (1907) ; *362*, 287 (1908).

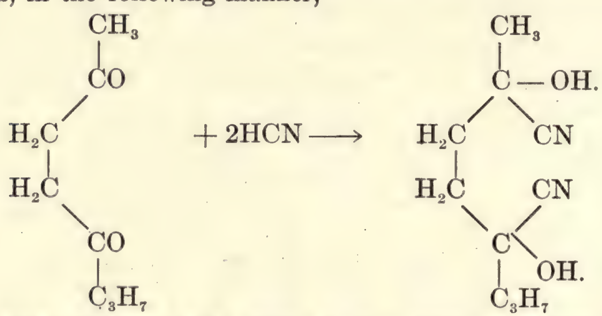
therefore not present in ordinary "terpinene" boiling at 179°–182° and which does not yield a crystalline tetrabromide. The constitution of "terpinene" therefore resolves itself into I or III, or a mixture of these two hydrocarbons.

On oxidizing ordinary terpinene with permanganate, α α′-dioxy-α-methyl-α′-isopropyladipic acid, melting-point 189° is formed. This acid can only be derived from $\Delta^{1.3}$-p-menthadiene.

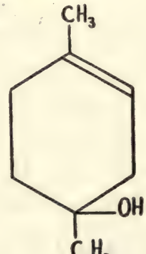


α-terpinene *erythrite* *adipic acid derivative*

The structure of this acid has been proved beyond question by its synthesis, in the following manner,



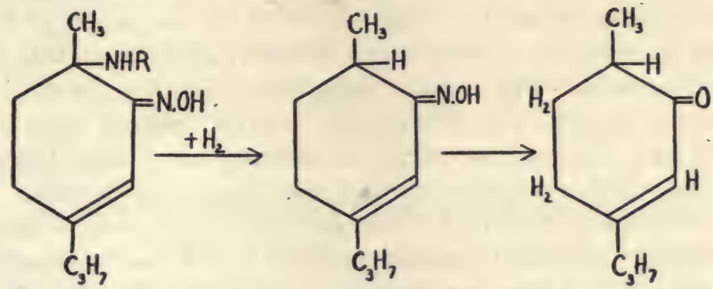
followed by hydrolyzing the nitrile to the adipic acid derivative. The structure of this acid can also be shown by following the oxidation of terpinenol-(4)



Terpinenol-(4)

which also yields this adipic acid derivative.[71] Further oxidation yields dimethyl-acetonylacetone whose dioxime melts at 137°.

Additional evidence of the presence of $\Delta^{1,3}$-p-menthadiene in "terpinene" has been furnished by the conversion of terpinene nitrosite to carvenone, first by reducing the nitrosite in alcohol solution by zinc,[72] and later with particularly good yields, by reducing the nitrolamine by zinc and acetic acid.[73]



terpinene nitrolamine *carvenone oxime* *carvenone*

In the investigation of terpinene from various different sources or made in different ways, it was observed that those specimens which give good yields of the α α′-dioxy-α α′-methylisopropyladipic acid, melting at 189°, also give good yields of the above crystalline nitrosite.[74] On the other hand it has been noted that specimens which yield little or no nitrosite also yield very little of the adipic acid derivative melting at 189°.

The presence of $\Delta^{1,4}$-p-menthadiene in terpinene was made practically certain by the discovery of Gildemeister and Müller[75] that one of the oxidation products was isopropyl tartronic acid. This specimen of terpinene was isolated from ajowan oil and Gildemeister and Müller were unable to isolate a crystalline nitrosite, nor could they detect the adipic acid derivative among the oxidation products. All experience with terpinene, particularly as brought out by Wallach's extensive investigations,[76] indicate that "terpinene" is a mixture containing varying proportions of the two isomers, which Wallach designates as α and γ-terpinene (see above). Auwers has studied the terpinene question from the standpoint of their physical properties, particularly the re-

[71] Wallach, *Ann.* *362*, 266 (1908).
[72] Amenomiya, *Ber.* *38*, 2730 (1905).
[73] Wallach, *Ber.* *40*, 582 (1907).
[74] Wallach, *Ann.* *374*, 229, 230 (1910).
[75] Schimmel & Co. Semi-Ann. Rep. *1909* (2), 16.
[76] *Ann.* *362*, 261, 285 (1908); *368*, 13 (1909); *374*, 224 (1910).

fractive index. In accord with Wallach's findings, Auwers showed that a terpinene having a particularly high refractive index, as would be expected in the case of α-terpinene, also gave a very large yield of crystalline nitrosite and the adipic acid derivative. Wallach believes that the preparation of strictly pure terpinenes, terpinolene and the phellandrenes is impossible.[77]

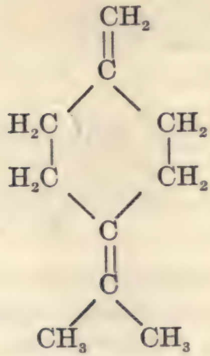
Carvenene is probably an impure α-terpinene. It was so named by Semmler,[78] who prepared it from carvenone by the action of PCl_5 followed by reduction. According to Semmler, alcoholic sulfuric acid converts carvenene to an isomeric hydrocarbon isocarvenene which he considers is identical with β-terpinene. Auwers does not agree with Semmler as to the supposed purity of carvenene and claims that it is not identical with α-terpinene which Auwers made from *O*-cresol.

Henderson and Sutherland [79] have made what appears to be mainly α-terpinene by reducing thymohydroquinone to 2.5-dioxy-p-menthane and decomposing this with removal of two molecules of water. Their α-terpinene showed a boiling-point of 179°, specific gravity about 0.840 and refractive index 1.4779. Pickles [80] isolated a terpene "origanene" from the volatile oil of *Origanum hirtum*, which he considers is probably α-terpinene.

Crithmene.

This terpene is mentioned in connection with the terpinenes since it yields terpinene dihydrochloride on treating with hydrogen chloride. It is contained in the volatile oil of *Crithmum maritimum*.[81] Its boiling-point is 178°–179°, specific gravity, 0.8658, $n\frac{20°}{D}$ 1.4806. It does not yield a crystalline tetrabromide, the nitrosite melts at 89°–90° and the nitrosate at 104°–105°. It yields two nitrosochlorides which can be distinguished by their different crystal forms, although the melting-points are very close together, 101°–102° and 103° and 104°. The discoverers have suggested that crithmene is probably $\Delta^{1\cdot(7)-4(8)}$-p-menthadiene.

[77] Fairly pure α-terpinene has been synthesized by Wallach, *Ber.* *42*, 2404 (1909).
[78] *Ber.* *41*, 4474 (1908) ; *42*, 522 (1909).
[79] *J. Chem. Soc.* *97*, 1616 (1910).
[80] *J. Chem. Soc.* *93*, 862 (1908).
[81] Fransesconi & Sernagiotto, *Atti accad. Lincei*, *1913*, 231, 312 ; Delepine & Belsunce, *Bull. soc. chim.* (4) *23*, 34 (1918).

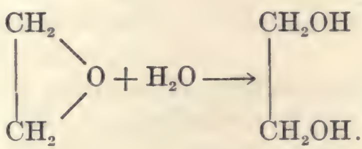


crithmene

The Oxides. 1.8-Cineol, 1.4-Cineol, Pinol and Ascaridol.

These oxides of the terpene series are usually described without reference to other intramolecular ethers, or oxides, of the non-benzenoid hydrocarbons. Unfortunately the number of such organic oxides, to use the customary term, which are known, is so small that it is not possible to show such close relationships between those which happen to have been first prepared from the terpenes, and those prepared from other non-benzenoid cyclic or open chain hydrocarbons, as might be desired.

In the first place it may be noted that the ethylene oxide ring is considerably less stable than the tri-carbon ring in cyclopropane and its derivatives. Thus ethylene oxide reacts with water on heating to give glycol and this reaction is catalyzed by a trace of a mineral acid.[82]



Oxides of this type have been carefully studied in the case of the oxides of ethylene, propylene, the butylenes, amylenes and hexylenes. They react with hydrogen chloride with considerable energy, forming the chlorohydrins; with ammonia to form the corresponding amino alcohols, with nascent hydrogen to give alcohols and with a variety of other substances, as, for example, sodium malonic ester,

[82] Henry, *Compt. rend.* *144*, 1404 (1907).

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O+\begin{array}{l}Na\\ \\ H\end{array}\!\!>C.(CO_2C_2H_5)_2\longrightarrow\begin{array}{l}CH_2ONa\\ |\\ CH_2CH(CO_2C_2H_5)_2.\end{array}$$

The greater instability of the ethylene oxide ring as compared with the tri-carbon ring is brought out in the case of isobutylenoxide $\begin{array}{c}(CH_3)_2C\text{——}CH_2,\\ \diagdown\ \ \diagup\\ O\end{array}$ which reacts with water to form the glycol merely on shaking together with water at ordinary temperatures. (The group $(CH_3)_2C<$ in cyclopropane usually results in greater stability.)[83] As with carbocyclic rings a great increase in stability is noted, compared wth ethylene oxide, when the oxide ring contains five or six atoms. Thus diethylene oxide $\begin{array}{l}CH_2-O-CH_2\\ |\qquad\qquad\ \ |\\ CH_2-O-CH_2\end{array}$ is the *principal* product resulting when ethylene glycol is distilled with 4 per cent aqueous sulfuric acid; in the same manner, but with smaller yields, 1.8-terpin yields ordinary cineol and 1.4-terpin yields 1.4-cineol. Diethylene oxide, in contrast to ethylene oxide, yields a series of well-defined addition products[84] of the type which Baeyer suggested were derivatives of quadrivalent oxygen; the sulfate, $C_4H_8O_2.H_2SO_4$ melts at 101°, the dibromide $C_4H_4O_2Br_2$ melts at 60°, etc. When the constitutions of these two substances are compared it is apparent that the reason for the greater stability of diethylene oxide is the hexatomic ring.

$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>O\qquad\qquad\qquad\begin{array}{l}CH_2-O-CH_2\\ |\qquad\qquad\ \ |\\ CH_2-O-CH_2\end{array}$$

diethylene oxide.

In connection with the stability of diethylene oxide its comparatively high melting-point + 9.5°, and boiling-point 100°–101° are significant. If the valence directions of quadrivalent oxygen are in the directions of the four corners of a regular tetrahedron as we assume to be the case in the carbon atom, then we should expect a close parallel with non-benzenoid carbocylic substances, as regards stability and ease of formation and rupture. Derick and Bissell[85] have called attention

[83] Ingold, *J. Chem. Soc. 119*, 305 (1921).
[84] Paterno & Spallino, *Gazz. chim. Ital. 37* (1), 196 (1907); Faworski, *Chem. Zentr. 1907* (1), 16.
[85] *J. Am. Chem. Soc. 1916*, 2478.

to the fact that trimethylene oxide $\underline{CH_2CH_2CH_2O}$, which contains four atoms in the ring is markedly more stable than ethylene oxide. [The stereochemistry of oxygen has been very little studied. There would seem to be no reason why substances containing asymmetric oxygen cannot be resolved into optically active forms, possibly by Pasteur's method of mechanically picking out crystals of opposite hemihedral development.] It has been noted[86] that 1.4 and 1.5-glycols and their oxides behave in a manner markedly different from the 1.2-glycols. The former are readily converted into their oxides of five and six membered rings respectively by heating with 60 per cent sulfuric acid and these oxides are quite stable to water; in fact, they can be heated with water to 200° several hours without forming glycols. It should be pointed out that their behavior is strictly parallel to the behavior of the better known oxides, cineol and pinol.

Up to the present time the only oxides whose synthesis has been attempted with the idea of industrial utilization are the simpler 1.2 oxides, i.e., ethylene oxide for the manufacture of phenylethyl alcohol by the Grignard reaction,[87]

$$C_6H_5MgBr + (CH_2)_2O \longrightarrow C_6H_5CH_2CH_2OH,$$

and other organic preparations,[88] and the 1.2 oxides of butylenes and amylenes which have been proposed as solvents for cellulose esters.[89] However, the 1.4 and 1.5 oxides are quite stable and should prove industrially valuable if they could be made economically.

Tetramethylene oxide.

$$\begin{array}{l} CH_2 - CH_2 \\ | \qquad\qquad\quad >O \\ CH_2 - CH_2 \end{array}$$

boils at 67° and is easily soluble in water. It is not reacted upon by water at 150° but is attacked by fuming hydrobromic acid.

1.4-*Oxidopentane.*

$$\begin{array}{l} CH_2 - CH - CH_3 \\ | \qquad\qquad\quad >O \\ CH_2 - CH_2 \end{array}$$

is a liquid of agreeable ethereal odor boiling at 77°–78° and soluble in 10 parts of water at ordinary temperatures. It can be made by heating the 1.4-glycol with 60 per cent sulfuric acid or by the action of caustic alkali on the

[86] Petrenko-Kritschenko & Konschin, *Ann.* *342*, 51 (1905).

[87] Grignard, *Compt. rend.* *136*, 1260 (1903); *Altwegg*, U. S. Pat. 1,315,619. According to the writer's experience this reaction gives yields 75 to 80 per cent. of the theoretical; ethylene oxide is best made by solid caustic soda on nearly anhydrous ethylene chlorohydrin.

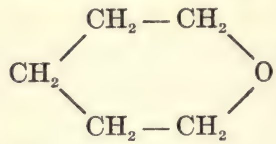
[88] Cf. *Soc. chim. du Rhone*, Brit. Pat. 128,552; 128,553; 128,554 (1919),—for aminobenzoic acid derivatives; Brit. Pat. 128,911 (1919) for chloroethyl esters; Brit. Pat. 128,908 (1919) for ethanolamines and aminophenol ethers.

[89] Walker, U. S. Pat. 972,952.

corresponding chlorohydrine. The dimethyl derivative is a product of the action of sulfuric acid on diallyl,

$$\begin{array}{l} CH_2CH=CH_2 \\ | \\ CH_2CH=CH_2 \end{array} \longrightarrow \begin{array}{l} CH_2CH-CH_3 \\ | \qquad\quad >O \\ CH_2CH-CH_3 \end{array} \qquad \text{boiling-point } 90^\circ\text{–}92^\circ$$

1.5-Oxidopentane (Pentamethylene oxide).[90]



can be obtained by heating 1.5-dibromopentane with water at 100° or from the glycol by the sulfuric acid method. The oxide boils at 81°–82°. The same methods of preparation have proven successful in the conversion of 1.4 and 1.5-dihydroxy-n.hexane[91] to the corresponding oxides. Most of the glycols containing six or more carbon atoms are quite difficult to prepare and since interest in them is so narrow, they are not described here. The above examples, however, are given in support of the general thesis of the present volume, that the chemistry of the so-called hydro-aromatic hydrocarbons is rationally a part of the larger division of non-benzenoid hydrocarbons.

Cineol is the name given by Wallach and Brass[92] to the substance $C_{10}H_{18}O$, boiling-point 172°, which they isolated from the volatile oil of wormseed, *"Oleum cinæ,"* from *Artemisia maritima L.* It was also shown that "cajeputol" from cajeput oil and "eucalyptol" were identical with cineol. Gladstone had shown that cineol could be distilled over metallic sodium without change and Hell and Ritter[93] obtained an addition product with hydrogen chloride and accordingly suggested that the oxygen was bound as in ethylene oxide, but recognized that cineol is much more stable than ethylene oxide.

The following additive compounds have been prepared from cineol, $(C_{10}H_{18}O)_2.HCl$; $(C_{10}H_{18}O)_2.Br_2$; $C_{10}H_{18}O.Br_2$; $(C_{10}H_{18}O)_2.I_2$; $C_{10}H_{18}O.HBr$; $C_{10}H_{18}O.H_3PO_4$; $C_{10}H_{18}O.H_3AsO_4$,[93] also well crystallized products with hydroferricyanic and hydroferrocyanic acids, α and β-naphthol,[94] iodol and resorcin. This property is utilized for the detection and quantitative estimation of cineol, methods based

[90] Hochstetter, *Monatsh.* 23, 1073 (1902).
[91] Franke & Lieben, *J. Chem. Soc. Abs.* 1913, I, 491.
[92] *Ann.* 225, 291 (1885).
[93] Merck, German Pat. 132,606.
[94] Henning, German Pat. 100,551; *Chem. Zentr.* 1899 (1), 764.

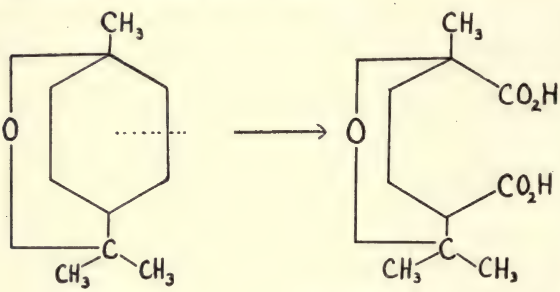
upon the reaction with phosphoric acid and with resorcin being most favored for quantitative estimation.[95]

Composition of Product[96]	*Melting-Point*
$C_{10}H_{18}O.HBr$	56. °
$C_{10}H_{18}O.C_4I_4NH$. (iodol)	112. °
$(C_{10}H_{18}O)_2.C_6H_4(OH)_2$ (resorcin)	80. °
$(C_{10}H_{18})_2.C_6H_4(OH)_2$ (hydroquinone)	106.5°
$C_{10}H_{18}O.C_6H_5OH$	8. °
$C_{10}H_{18}O.C_6H_4OH.CH_3$ (orthocresol)	50. °
$C_{10}H_{18}O$. thymol	4.5°

Baeyer[97] first pointed out that these addition products, which are generally decomposed easily into their original constituents, are probably derivatives of quadrivalent basic oxygen. Baeyer regarded the comparatively stable compound of ethyl ether and magnesium-alkyl halides as "oxonium" compounds of the constitution $(C_2H_5)_2O{<}^{X}_{MgR}$ but more recent investigations point to the structure $\begin{matrix} C_2H_5 & & MgX \\ & {>}O{<} & \\ C_2H_5 & & R \end{matrix}$ which was proposed by Grignard. When cineol is used as a reaction medium instead of ether, the reaction of magnesium, ethyl iodide and cineol takes place with almost explosive violence unless the cineol is diluted with benzene.[98] When cineol is added to a solution of magnesiumethyl iodide in ethyl ether, the ethyl ether is displaced and the cineol compound, $(C_{10}H_{18}O)_2MgC_2H_5I$, is precipitated. When this compound is decomposed by dilute acids cineol is almost quantitatively regenerated, but if the complex is heated to 170°–190° and then carefully decomposed by cold dilute acids, α-terpineol is formed. If the conditions are reversed and magnesium-ethyl-bromide is poured into cineol, an oil is produced the products of hydrolysis of which have not been investigated. 1-Ethyl-p-menthanol(8) should be formed if the reaction product, like many other Grignard ether complexes which have been investigated, is capable of decomposing in several ways. In the case of ethylene oxide and phenyl magnesium bromide, phenyl ethyl alcohol is the principal product. Cineol reacts with acetic anhydride in the presence of metallic chloride $ZnCl_2$ or $FeCl_3$ to form terpinyl acetate and terpin diacetate.[99]

[95] Cf. Parry, "Chemistry of Essential Oils," Ed. 3, Vol. I, 321, Vol. II, 256; Gildemeister, "Aetherische Oele," Ed. 2, Vol. I, 547.
[96] Belluci & Grassi, *Chem. Zentr.* *1914* (1), 884.
[97] *Ber.* *34*, 2679 (1901); *35*, 1201 (1902).
[98] Pickard and Kenyon, *J. Chem. Soc. 91*, 896 (1907).
[99] Knoevenagel, *Ann.* *402*, 111 (1919).

The constitution of cineol is clearly indicated by its formation from 1.8-terpin by oxalic acid and other dehydrating agents, by the formation of dipentene dihydrochloride from cineol by the action of hydrogen chloride (in acetic acid), by the absence of a double bond and the absence of a carbonyl group. Cineol was formerly regarded as the 1.4 oxide but when α-terpineol was shown to be Δ^1-p-menthenol (8) and ordinary terpin to be the 1.8 derivative, the constitution attributed to cineol was revised to accord with these facts. Hot permanganate solution oxidizes cineol to cineolic acid, which substance retains the 1.8 oxide grouping.



cineol *cineolic acid, M.-P.* 197°

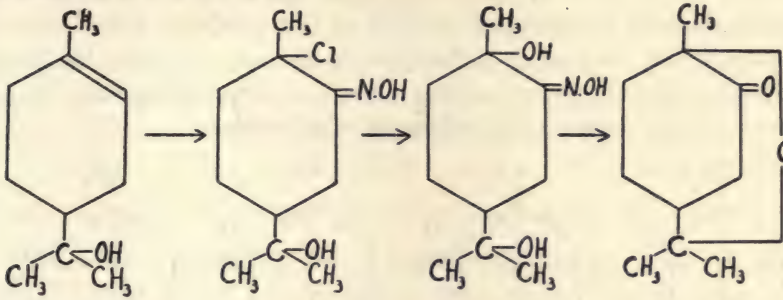
Cineol occurs in the volatile oil of many species of eucalyptus and the commercial valuation of eucalyptus oils is usually determined by their cineol content. Commercial oils are derived from a number of different species and earlier references to the essential oil of *Eucalyptus globulus* undoubtedly refer to the mixed oil from several species. The genuine oil of *Eucalyptus globulus* contains 50 to 70 per cent of cineol, the balance being *d-α-pinene,* and minor percentages of a sesquiterpene alcohol which has been named globulol, an unidentified terpene and very small proportions of butyric, valeric and caproic aldehydes. R. T. Baker and H. G. Smith have made a systematic survey of the various species of eucalyptus and the volatile oils derived from them, the results of which have been published in a comprehensive monograph [100] and in a series of papers in the *Journal of Proceedings,* Royal Society of New South Wales. Baker and Smith find 58 species yielding oils whose principal constituents are cineol and pinene, 14 in which pinene and sesquiterpenes are the chief components, 9 which contain notable percentages of a new aldehyde "aro-

[100] "Eucalypts of Tasmania," 1912; *J. Soc. Chem. Ind.* 32, 710 (1913).

madendral,"[101] 33 species which yield oils characterized by phellandrene and piperitone (q.v.), and several other species whose oils differ markedly from those above mentioned.[102]

Cineol crystallizes on chilling the fraction boiling at 174°–178° from good eucalyptus oil and its isolation in this way is comparatively easy, though naturally not quantitative.

A ketone derivative of cineol has been made from α-terpineol by first preparing α-terpineol nitrosochloride, treating this with hydroxylamine, thus replacing Cl by —NH.OH. and hydrolyzing the resulting product by water.[103]



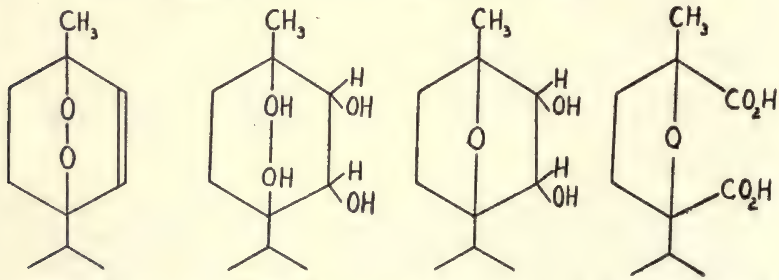
α-*terpineol*

1.4-Cineol: This isomer of ordinary cineol has not been found in nature, but was discovered by Wallach as one of the products of the dehydration of 1.4-terpin by oxalic acid.[104] It boils at 172° but does not crystallize on cooling to —15°. It is quite stable to permanganate solution.

Ascaridol is one of the most remarkable organic compounds known. It was discovered by Schimmel & Co. in 1908[105] in the volatile oil of American wormseed or *Chenopodium ambrosioides*, L., *var anthelminticum.* It was found to contain two atoms of oxygen and on heating to 130°–150° decomposes with explosive violence. On reducing by Paal's method, four atoms of hydrogen are taken up and one of the stereoisomeric forms of 1.4-terpin are formed. This 1.4-terpin, melting at 116°–117°, is regarded by Wallach[106] as the *cis* form. (The identity of this terpin was clearly shown by its conversion to terpinene dihydrochloride and by its decomposition to 1.4-cineol.)

[101] *J. Proc. Roy. Soc. N. S. W.* 1900, 1.
[102] An excellent review of the eucalyptus oils is given in Parry, "Chemistry of Essential Oils," Ed. 3, Vol. I, pp. 319-358.
[103] Cusmano & Linari, *Gazz.* *42* (1), 1 (1912).
[104] *Ann.* *392*, 62 (1912).
[105] Reports, *1908* (1), 108.
[106] *Ann.* *392*, 59 (1912).

The absence of double bonds and hydroxyl or carbonyl oxygen, its *peroxide*-like properties and its relation to 1.4-terpin, indicates, in Wallach's opinion, a peroxide structure. Nelson[107] first showed the peroxide character of ascaridol but suggested that the two peroxide oxygen atoms connected the 2.5 positions. By treating with ferrous sulfate solution in the cold two glycols $C_{10}H_{18}O_3$, melting at 62.5°–64° and 103°–104° are obtained. Heating the higher melting glycol with dilute sulfuric acid yields p-cymene. According to Wallach's constitution for ascaridol, the erythritol $C_{10}H_{20}O_4$, melting at 128°–130° should yield α, α′-methyl-isopropyl-α, α′-dihydroxyadipic acid, and Nelson obtained an oxidation product of this acid, i.e., 2-methylheptane-3.6-dione. By acid permanganate Nelson has split the acid $C_{10}H_{16}O_5$, from the lower melting glycol, to 2-methyl-heptane -3.6-dione. Nelson suggests the following relationships.



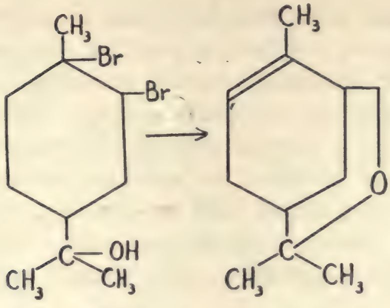
ascaridol *erythritol* *glycol* *1.4-cineolic acid*

Ascaridolic acid, which possesses the structure of a 1.4-cineolic acid, was resolved by Nelson by means of its cinconidine salt to the *d.* and *l.* forms.

The physical properties of ascaridol are, boiling-point 83° under 5 mm. pressure, sp. gr. (20°) 1.008, $[\alpha]_D$ —4° 14 and $n_D^{20°}$ 1.4731.

Pinol: The resemblance of pinol to the two cineols is indicated by its chemical behavior and its methods of preparation. Thus terpineol dibromide,[108] on treating with aniline or alcoholic alkali loses one molecule of hydrogen bromide to form an unsaturated bond and loses a second molecule of HBr after the fashion of the bromo-hydrines and chlorohydrines to form the oxide pinol.

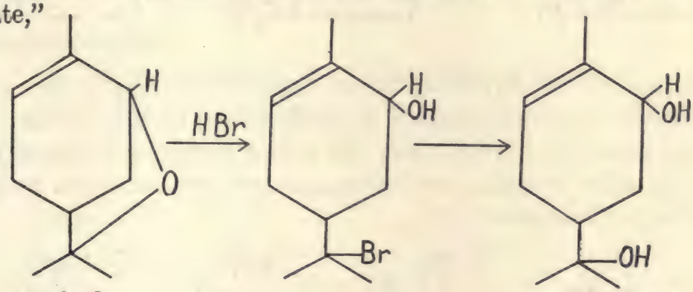
[107] *J. Am. Chem. Soc.* *33*, 1404 (1911); *35*, 84 (1913).
[108] Wallach, *Ann.* *253*, 254, 261 (1889).



α-terpineol dibromide *pinol*

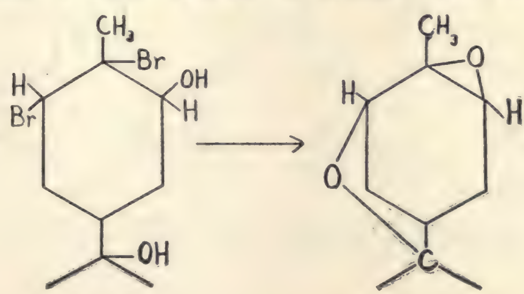
Like cineol the oxide ring is quite stable but the double bond reacts normally, being oxidized by permanganate to terebinic acid, adds bromine to form pinol dibromide, melting-point 94°, gives a nitrosochloride, etc. The odor of pinol resembles cineol and camphor. With mineral acids it readily yields cymene. Its physical properties are as follows, boiling-point 183°–184°, $d\frac{20°}{}$ 0.942, $n\frac{20°}{D}$ 1.4714.

When pinol is treated with hydrogen bromide in acetic acid solution, the oxide ring is broken, as with other oxides, and so-called pinol hydrobromide is formed, which on treating with alkali yields "pinol hydrate,"

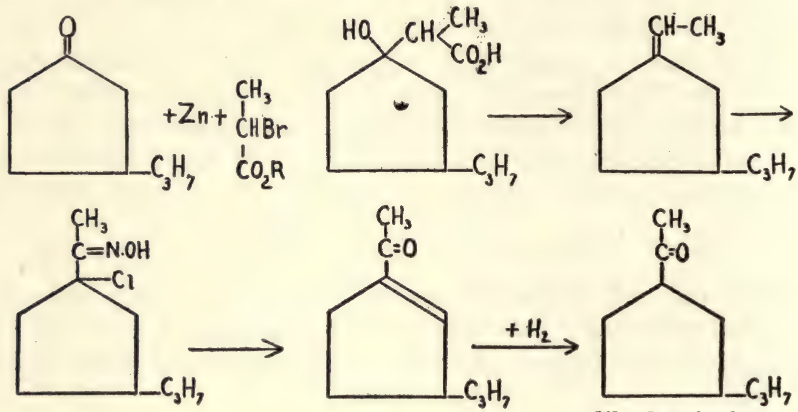


pinol *pinol hydrate*

The dibromide of pinol hydrate on treating with alkali yields a *dioxide,*

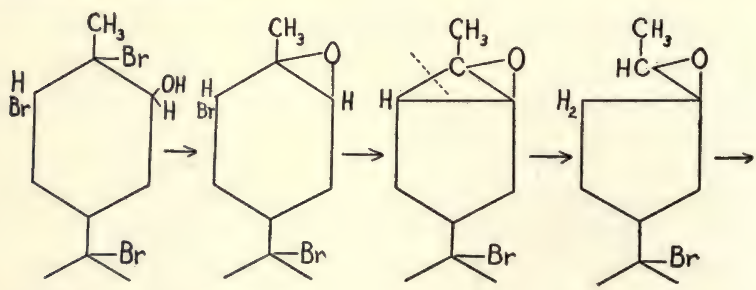


On treating pinol tribromide with zinc in acetic acid *pinolone* is formed. This reaction has been a puzzling one and is worth noting as an instance, now established beyond question, of the conversion of the six carbon ring to the cyclopentane ring. Wallach [109] has proven that dihydropinolone is acetylisopropylcyclopentane. Hydrogenation of pinolone yields the saturated ketone dihydropinolone, the constitution of which has been shown both by decomposition studies and by synthesis, to be 1.3-acetylisopropylpentanone. The synthesis is of interest as employing reactions of quite general application.



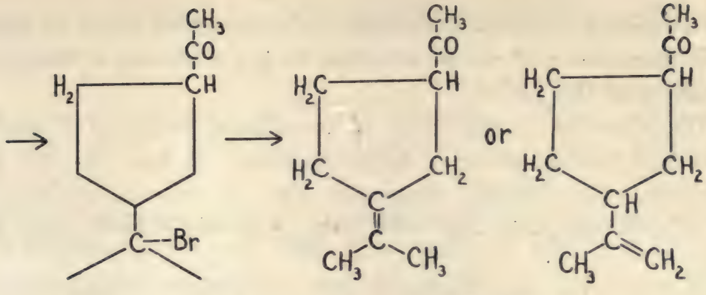
dihydropinolone

The fact of the formation of the cyclopentane ring is thus clearly established. Wallach suggests an explanation of this change which is based upon the conversion of the glycid group to a ketone group, many examples of which are known, particularly as shown by recent researches of Darzens.[110]



pinol tribromide

[109] *Ann. 384,* 193 (1911).
[110] *Compt. rend. 152,* 443, 1105 (1911).



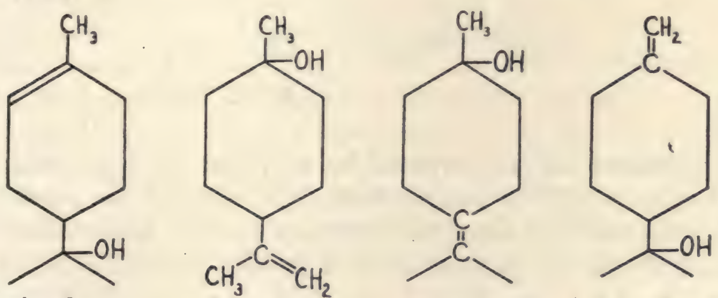
pinolone

As mentioned above, chlorohydrines yield oxides when treated with caustic alkali. Slawenski [111] has made pinol and pinol hydrate by the action of caustic potash upon the chlorohydrin of terpineol (the latter substance being made by the direct addition of hypochlorous acid to terpineol). The formation of pinol and pinol hydrate shows that the chlorine is in position 6.

An oxide of the diterpene series has been discovered in Java, citronella oil. The oxide, $C_{20}H_{34}O$, boils at 182°–183° (at 12 mm.). It contains two double bonds and is reduced by hydrogen and platinum black to $C_{20}H_{38}O$: it yields a monohydrochloride melting at 107.5°. When citronellal is heated with oxalic acid, one of the products is an isomeric oxide $C_{20}H_{34}O$.[112]

Other Alcohols of the Paramenthane Series.

It is evident that by the partial decomposition of ordinary terpin or terpin hydrate, four isomeric terpineols can theoretically be produced, i.e.,



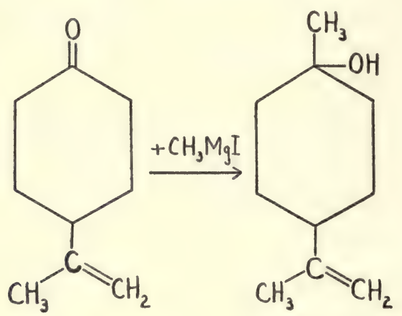
α-*terpineol*	β-*terpineol*	γ-*terpineol*	δ-*terpineol*
Inactive M.-P. 35°	*M.-P.* 32°	*M.-P.* 69°–70°	(unknown)
Active M.-P. 37°–38°			

[111] *Chemik. Polski,* 15, 97 (1917); *Chem. Abs.* 13, 887 (1919).
[112] Semmler, *Ber.* 47, 2077 (1914); Spornitz, *Ber.* 47, 2478 (1914).

α-*Terpineol* has been described in the foregoing pages on account of the importance of its constitution to the structure of the related substances of this series.

β-*Terpineol* is a constituent of commercial terpineol [113] made by the partial decomposition of terpin hydrate. It has not been found in nature. Its physical properties are as follows, melting-point 32°–33°, boiling-point 209°–210°, $d_{15°}$ in supercooled state 0.923, $n\frac{20°}{D}$ 1.4747. Its phenylurethane melts at 85°, the nitrosochloride at 103°,[114] the nitrolaniline derivative at 110° and the nitrolpiperidine derivative at 108°.

β-Terpineol was made synthetically by Perkin,[115] in a manner which clearly confirms its structure. Incidental to the synthesis of α-terpineol, described above, a small amount of hydroxyisopropylcyclohexane-4-one was formed, which ketone was dehydrated in the usual manner. When the resulting unsaturated ketone was treated with magnesium-methyl iodide, β-terpineol was formed.

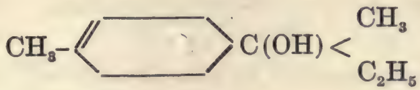


β-*terpineol*

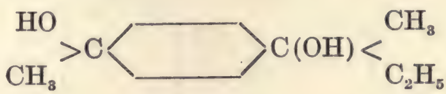
The decomposition of β-terpineol by oxidation has been studied by Stephan and Helle [116] and by Wallach.[117] One of the products of oxidation, 1-methyl-4-acetyl-Δ^1-cyclohexene has been utilized by Wallach [118] for the preparation of a number of saturated and un-

[113] Schimmel & Co. Semi-Ann. Rep. 1901 (1), 79; Stephan & Halle, Ber. *35*, 2147 (1902).
[114] Wallach, *Ann. 345*, 128 (1903).
[115] *J. Chem. Soc. 85*, 659 (1904).
[116] *Loc. cit.*
[117] *Ann. 324*, 88 (1902).
[118] *Ann. 414*, 202 (1918).

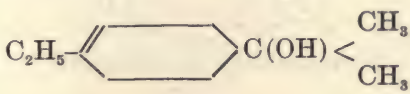
saturated alcohols. Thus magnesium-ethyl iodide yields homo-α-terpineol



Nascent hydrogen reduces the carbonyl group and when the resulting product is treated with dilute sulfuric acid 1.8-dihydroxy-1-methyl-4-ethylcyclohexane, melting at 94°, is formed. Two other 1.8-terpins were described in the same paper, i.e., addition of water to homo-α-terpineol yields



melting-point 65°–67°, and secondly hydration of



by dilute acids gave the corresponding 1.8-terpin, crystallizing with one molecule of water, melting at 75°–76°.

γ-*Terpineol* has not been found in nature, but is one of the minor reaction products when ordinary 1.8-terpin is partially decomposed by oxalic or phosphoric acids. It was prepared by Baeyer incidental to his investigation of the constitution of terpinolene (q.v.). It is characterized by its relatively high melting-point, 69°–70°, and its blue nitrosochloride melting at 82°. On heating with about one volume of concentrated formic acid terpinolene results.[119]

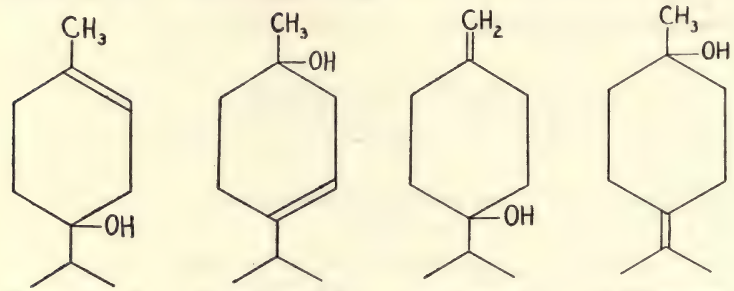
Δ^3-*p-Menthenol*(8), was made synthetically by Perkin and Wallach[120] incidental to their synthesis of $\Delta^{3 \cdot 8(9)}$-p-menthadiene. It melts at 41°, boils at 205° with slight decomposition and yields a phenylurethane melting at about 128°, the melting-point varying somewhat with the rate of heating owing to decomposition at this temperature.

Δ^2-*p-Menthenol*(1), is related to the phellandrenes (q.v.). It is

[119] Wallach, *Ann.* 368, 11 (1909).
[120] *Ann.* 374, 198.

easily decomposed by dehydrating agents to give α-phellandrene. It was made synthetically by Wallach[121] by the action of magnesium methyl iodide on 4-isopropyl-Δ^2-cyclohexenone. It boils at 92° (10 mm.).

The Terpinenols: Several terpene alcohols are known which can be derived from the 1.4-terpin of the terpinene series, and are hence called terpinenols. As in the case of 1.8-terpin, noted above, loss of one molecule of water from 1.4-terpin can theoretically lead to the formation of four isomeric alcohols.



Terpineol-4 *Terpinenol-1* unknown γ-*Terpineol*

Of the substances indicated above, it will be noted that IV is identical with γ-terpineol.

Terpinenol-4 is found in nature in a number of essential oils, juniper, Ceylon cardamon, nutmeg and zedoary.[122] It is formed by the hydration of sabinene by cold dilute sulfuric acid.[123] The physical properties of optically active terpinenol-4 are as follows, boiling-point 209°–212°, $d_{19°}$ 0.9265, $[\alpha]_D$ $+25°\ 4'$, $n\frac{19°}{D}$ 1.4785. It has not been obtained in crystalline form. Both terpinenol-4 and terpineol-1 give terpinene dihydrochloride when treated with hydrogen chloride in glacial acetic acid, and also give 1.4-terpin on hydrating with cold, dilute sulfuric acid, although this hydration takes place much more slowly than with α-terpineol. The two terpinenols are however distinguished by their oxidation products,[124]

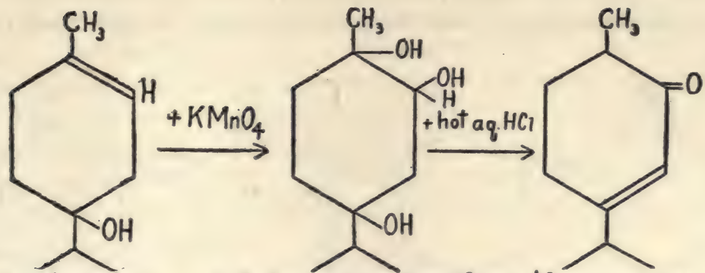
[121] *Ann. 359*, 283 (1908).

[122] Terpinenol — 4 is present in comparatively large proportions in one of the Formosan lauraceæ closely resembling the camphor tree; Schimmel & Co. Semi-Ann. Rep. 1915 (2), 42.

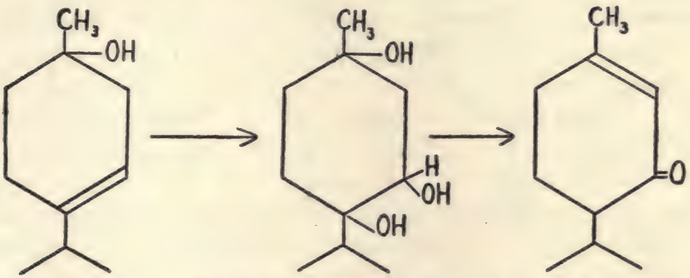
[123] Wallach, *Ann. 360*, 94, 97 (1908); *362*, 279 (1908).

[124] Wallach, *Ann. 356*, 210 (1907).

(a)



terpinenol-4 (Δ^1-*p-menthenol 4*) *1.2.4.-trioxy-p-menthane* *M.-P.* 116°–117° (H_2O). Δ^3-*carvenone*



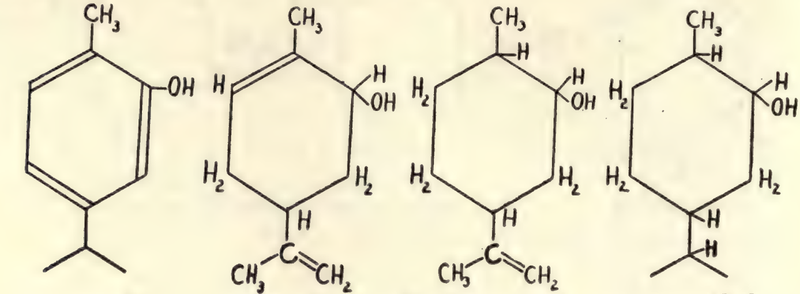
terpinenol-1 *1, 3, 4-trioxy-p-menthane* *M.-P.* 120°–121° Δ^1-*menthenone* [125]

Terpinenol-1 occurs in commercial terpineol and can be isolated from the forerunnings obtained when large quantities of crude terpineol are distilled with steam. It has also been synthesized by the action of magnesium methyl iodide on Δ^3-4-isopropyl cyclohexenone. Its physical properties [126] are as follows, boiling-point 208°–210°, $d_{18°}$ 0.9265, and $n\frac{18°}{D}$ 1.4781.

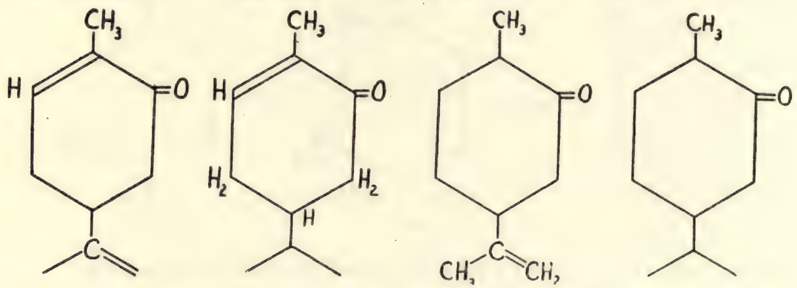
Dihydrocarveol, $\Delta^{8(9)}$-p-menthenol(2), is found in nature in oil of caraway, associated with carvone. Its importance in the work of determining the constitutions of limonene and related substances has already been pointed out. It can be made by the reduction of carvone by sodium and alcohol,[127] or by the reduction of carvoxime to dihydrocarvylamine and treating the latter with nitrous acid. Complete

[125] Δ'-p-menthenone is characterized by its boiling-point 235°-237°, the oxime melting at 77°-79° and its semicarbazone melting at 210°.
[126] Wallach, *Ann.* *356*, 218 (1907).
[127] Wallach, *Ann.* *275*, 111 (1893).

reduction yields carvomenthol.[128] The relationships between the more important substances of this carvone series may be indicated as follows,



carvacrol *carveol* *dihydrocarveol* *carvomenthol*



carvone *carvotanacetone* *dihydrocarvone* *tetrahydrocarvone*

Dihydrocarveol is characterized by oxidation by chromic acid to dihydrocarvone, whose oxime melts at 88°–89° (inactive) or 115°–116° (active form), and by its physical properties,[129] boiling-point 224°, d_{15° 0.9368, and $n_{D}^{20^\circ}$ 1.4836. By shaking with 3 per cent sulfuric acid it is hydrated to 2.8-dioxy-p-menthane (M.-P. 112°–113°).

Carveol is one of the principal products of the oxidation of limonene by air in the presence of water.[130] It boils at 226°–227°, yields a phenylurethane melting at 94°–95°, and a phthalate melting at 136°–137°. Its methyl ether (by CH_3ONa on 1,2,8-tribromomenthane) boils at 208°–212.°

Isopulegol, $\Delta^{8(9)}$-p-menthenol(3). This alcohol is not found in nature but is readily formed from citronellal by the action of acids;

[128] Cf. Henderson & Schotz, *J. Chem. Soc. 101*, 2565 (1912).
[129] Schimmel & Co. Semi-Ann. Rep. 1905 (1), 51.
[130] Blumann & Zeitschel, *Ber. 47*, 2623 (1907).

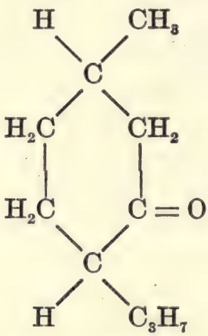
when oils containing citronellal are heated with acetic anhydride this aldehyde is almost quantitatively converted into the acetate of isopulegol. Heating with sodium ethoxide[131] converts isopulegol to citronellol and also decomposes it to acetone and methylcyclohexanol (3). Isopulegol is characterized by oxidation to the corresponding ketone, isopulegone,[132] which ketone yields an oxime melting at 121° (active) and 140° (inactive form). The acetate boils at 104°–105° under 10 mm. pressure. Isopulegol boils at 91° under 13 mm. pressure, $d_{17.5°}$ 0.9154, n_D 1.4729.

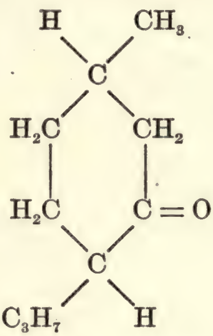
Menthol, para-menthanol(3). This saturated alcohol is a common article of commerce. Up to the present it has not been manufactured synthetically but is obtained from oil of peppermint, particularly Japanese peppermint. Peppermint has been under cultivation in Japan since about 900 A.D., and in Europe for a period probably equally long, and, as is usually the case with cultivated plants, there are numerous varieties and the number of distinct species is as yet an open question. Yet, with the exception of oil of spearmint[133] which is characterized by considerable proportions of carvone, the various peppermint oils owe their characteristic flavor and aroma to menthol and the corresponding ketone menthone. The menthol occurs in these oils partly free and partly in the form of esters of acetic and other acids, and on chilling part of the free menthol crystallizes from the oil. The melting-point of menthol is 42.5°. According to F. E. Wright,[134] ordinary *l*.menthol crystallizes in four different forms, α, β, γ and δ, only one of which, the α-form, is stable between zero and its melting-point, 42.5°. The other three forms are monotropic and have lower melting temperatures, i.e., 35.5° β, 33.5° γ, and 31.5° δ; all the unstable forms invert finally into the stable α-form. Previous work of Schaum,[135], Pope,[136] Hulett[137] and others had shown the existence of at least two unstable forms, which investigations were confirmed and extended by Wright. Menthol boils at 215°–216°, $d.\frac{45°}{4°}$ 0.881 and when derived from peppermint is lævorotatory. Pick-

[131] Schimmel & Co. Semi-Ann. Rep. 1913 (2), 91.
[132] Wallach, *Ann.* *365*, 251 (1909).
[133] In the United States oil of spearmint is derived from *Mentha viridis* (Mentha spicata). The peppermint oil industry is very fully described by Parry, "Chemistry of Essential Oils," Ed. 3, Vol. I, 205-231.
[134] *J. Am. Chem. Soc.* *39*, 1515 (1917).
[135] *Ann.* *308*, 39 (1899).
[136] *J. Chem. Soc.* 75, 463 (1899).
[137] *J. Phys. Chem.* *28*, 667 (1899).

ard and Littlebury[138] made menthol by the catalytic hydrogenation of thymol, and by resolution of the brucine salt of the monomenthylphthalic ester *l.*menthol was obtained $[\alpha]_D - 48.76°$ and *d.*menthol $[\alpha]_D + 48.15°$. A very large number of menthyl esters have been employed in the study of optical activity.[139]

On oxidation, menthol is converted into the corresponding ketone menthone, p-menthane-3-one. The relationships between menthol and menthone have been made clear by the work of Pickard and Littlebury. A ketone of this structure should exist in two stereoisomeric forms of the *cis* and *trans* type and these have usually been referred to as menthone and isomenthone.[140] Since each of these ketones contains an asymmetric





carbon atom, each should correspond to a pair of optically active isomerides, and when the carbonyl group is reduced to $>C<\substack{H \\ OH}$ the possible number of optically *inactive* isomerides is increased to four and the number of optically *active* isomerides to eight. By the hydrogenation of thymol in the presence of catalytic nickel, which had been carried out by Brunel,[141] a mixture containing 60 per cent of "menthols," 30 per cent of menthones and 10 per cent of unchanged thymol is obtained. After removing the thymol, the alcohols were separated by phthalic anhydride, in the usual manner. The semibarbazones of the mixture of menthones proved to have widely different solubilities in alcohols, one nearly insoluble in cold alcohol

[138] *J. Chem. Soc. 101,* 109 (1912).
[139] Tschugaeff, *Ber. 31,* 360 (1898); Cohen, Woodroffe & Henderson, *J. Chem. Soc. 109,* 222 (1916); Rupe, *Ann. 395,* 87, 136.
[140] This nomenclature was used by Aschan, "Chemie d. alicyklischen Verbindungen," *1905.*
[141] *Compt. rend. 140,* 252 (1905), *et seq.*

and melting at 217°, previously described by Wallach,[142] and a more soluble one melting at 158°. Fractional crystallization of the hydrogen phthalate esters yielded two pure products, one melting at 177° and one melting at 130°. The ester melting at 177° on hydrolysis yields an optically inactive menthol melting at 51°, "neomenthol," previously isolated by Beckmann.[143] Hydrolysis of the menthyl hydrogen phthalate melting at 130° yields an inactive menthol melting at 34°, which can be resolved, by means of the cinchonine or brucine salt, to ordinary *l*.menthol, melting-point 43°, and *d*.menthol, melting-point 43°. These relations are evidently parallel to and of the same nature as those between the borneols, isoborneols and camphors (q.v.). The following diagram summarizes the findings of Pickard and Littlebury,

Thymol,

menthone semicarbazone M.-P. 158° | *iso*menthone semicarbazone M.-P. 217°

i-Menthol, M.-P. 34° (hydrogen phthalate, M.-P. 130°) | *i-neo*-menthol, M.-P. 67° (hydrogen phthalate, M.-P. 177°)

1-menthol M.-P. 43° $[\alpha]_D$ —48.76° | *d*. menthol M.-P. 43° $[\alpha]_D$ +48.15° | *d*. neomenthol oil $[\alpha]_D$ +19.6° | 1.neomenthol oil $[\alpha]_D$ —19.6°

by oxidation

l-menthone | *d*-menthone

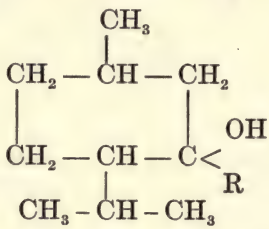
By the hydrogenation of pulegone by the Sabatier and Senderens method, Haller and Martine[144] obtained two menthols which evi-

[142] *Ann.* *263,* 272 (1908).
[143] *J. prakt. Chem.* (2) *55,* 30 (1897).
[144] *Compt. rend.* *140,* 1298 (1905). Haller's β-pulegomenthol is probably d-neomenthol and his α-pulegomenthol evidently belongs to the isomenthol series.

dently are identical with *l*.menthol and *d*.neomenthol described above. By electrolytic reduction of menthone in solution in about equal parts of 94 per cent alcohol and 75 per cent sulfuric acid a yield of 25 per cent of the theory of menthol has been reported.[145] Beckmann[146] has described an isomenthol melting at 78°–81°, obtained by the reduction of a specimen of *d*.menthone made by inverting *l*.menthone by 90 per cent sulfuric acid.

By passing synthetic menthol (from thymol) over copper at 300°, it is converted to menthone.[147]

Substituted menthols of the general constitution indicated below have been made from menthone by the Grignard reaction, and by zinc and alkyl halides,



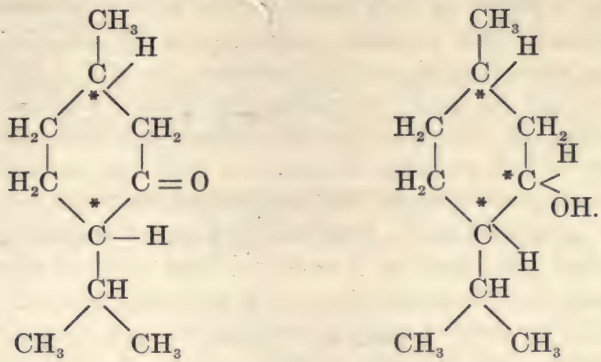
Magnesium cyclohexyl bromide[147] gives the cyclohexyl derivative melting at 92° together with a cyclohexylmenthene boiling at 265°. Methyl iodide and magnesium give chiefly the methyl tertiary alcohol, but ethyl iodide and magnesium or zinc yields chiefly a hydrocarbon $C_{12}H_{22}$.[148] Allyl iodide and zinc[149] give the expected allyl derivative, boiling-point 246°–252°.

Hallers' reaction has been employed by Boedtker[150] for the preparation of alkyl derivatives of menthone in which the alkyl groups are in position *2*. Thus ethyl iodide and sodium amide, reacting with menthone, give 2-ethyl-p-menthanone(3) from which by reducing in moist ether by sodium the 2-ethyl menthol was made. The methyl, *n*-propyl, isoamyl and benzyl derivatives were prepared in the same manner.

The stereochemistry of substances such as menthone and menthol is somewhat involved and has led to some confusion in the description

[145] Matsui, *J. Soc. Chem. Ind. 1921,* 162A.
[146] *Ber. 42,* 846 (1909).
[147] Murat, *J. Chem. Soc. Abs. 100* (1), 890 (1911).
[148] Vanin, *J. Chem. Soc. Abs. 100* (1), 474 (1911); *J. Russ. Phys.-Chem. Soc. 44,* 1068 (1912).
[149] Saytzeff, *J. Chem. Soc. Abs. 100* (1), 474 (1911); Ryschenko, *J. Russ. Phys.-Chem. Soc. 41,* 1695 (1909).
[150] *Bull. Soc. chim.* (4) *17,* 360 (1915); Haller, *Compt. rend. 156,* 1199 (1913). Dimethylmenthone ⟶ dimethylmenthol, a liquid boiling at 245°-247°.

of these substances and their derivatives. It should be pointed out that aside from *cis-trans* relationships discussed above, menthone possesses *two* and menthol *three* asymmetric carbon atoms.



Theoretically, therefore, menthol should be capable of existing in four spatial configurations of which each would have two optical antipodes and one racemic form. Kursanov [151] finds that when ordinary menthol is treated with phosphorus pentachloride, in benzene solution, a mixture of menthyl chlorides is obtained, which are of markedly different stability to caustic alkali. The stable chloride reacts with magnesium in ether to give a menthene, para-menthane, a crystalline dimenthyl $(C_{10}H_{19})_2$ melting at 105°–106°, $[\alpha]_D$ — 51.42° (which is identical with the dimenthyl obtained by the action of metallic sodium on this chloride) and when the menthyl-magnesium chloride thus formed is treated with carbon dioxide, a crystalline menthanecarboxylic acid results. The unstable menthyl chloride yields a liquid menthanecarboxylic acid and the crude menthyl chloride consequently must contain two stereoisomers. Kursanov concludes that only the carbon atom (3) attached to the hydroxyl group in the original menthol is inverted by the reaction. When *l*.menthone, corresponding in spatial configuration to ordinary *l*.menthol, is treated with 90 per cent sulfuric acid, it is partially inverted to *d*.isomenthone and according to Beckmann [152] the asymmetric carbon atom involved in the change is the one to which the isopropyl group is attached.

When the potassium derivative of menthol is heated with phenyl bromide or iodide the products are benzene and menthone, but in the

[151] *J. Chem. Soc. Abs.* *108* (1), 420 (1915).
[152] *Ber.* *42*, 846 (1909).

presence of finely divided copper the reaction gives a high yield of menthylphenyl ether. When this ether is heated with concentrated hydrochloric acid to 170° this ether is isomerized to menthyl phenol.

Menthol is relatively very stable and its esters can accordingly be easily prepared. The benzoate, melting-point 54°, can be prepared by heating with benzoic acid in autoclave to 170°. Although the benzoate cannot be made by mixing the alcohol with benzoic and sulfuric acids, the phenyl acetate and phenyl propionate can be made in this way.[153] In studying the action of esters on magnesium alkyl halides Stadnikow[154] found that magnesium menthyl iodide reacts with ethyl acetate to give a practically quantitative yield of menthyl acetate; ethyl propionate gave an 80 per cent yield of menthyl propionate and ethyl benzoate gave 64.6 per cent menthyl benzoate. Tschugaeff[155] prepared a series of menthyl esters by acting upon menthol by various acid chlorides in slight excess. A great many esters of menthol have been employed in the study of optical activity. The following table gives the boiling-point or freezing-point of a number of menthyl esters.

Ester	*Melting-Point*	*Boiling-Point*		*Density*
				20°
Formate	......	98. °	(15mm.)	0.9359
				4°
Acetate	......	108. °	"	0.9185 "
Propionate	......	118. °	"	0.9184 "
Butyrate	......	129. °	"	0.9114 "
Valerate	......	141. °	"	0.9074 "
n.Hexoate	......	153. °	"	0.9033 "
n.Heptoate	......	165. °	"	0.9006 "
n.Octoate	......	175. °	"	0.8977 "
Dimenthyl oxalate	67. °–68.°	......		......
Dimenthyl succinate	62. °	......		......
Menthyl-H-phthalate	110. °	......		......
Dimenthyl phthalate	133. °	......		......
Dimenthyl muconate	168. °	......		......
Dimenthyl β, γ-hydromuconate	79. °	......		......
Dimenthyl, α, β-hydromuconate	83. °	......		......
Dimenthyl adipate	61. °	......		......
Menthyl piperate	83. °	......		......
Menthyl β, γ-hydropiperate	......	263. °	(25mm.)	......
Menthyl α, β-hydropiperate	......	270. °	"	......
Dimenthyl malonate	62. °	......		......
Menthyl glutarate	......	240-3°	(20mm.)	......
Menthyl pimelate	......	248. °–252.°	(20mm.)	......
Menthyl suberate	......	257-9°	(20mm.)	......
Menthyl azelate	......	254.6°	(20mm.)	......
Menthyl sebacate	......	256. °–258.°	(20mm.)	......
Menthyl benzoate	54.5°	......		......

[153] Senderens & Aboulenc, *Compt. rend.* *155*, 1254 (1912).
[154] *J. Russ. Phys.-Chem. Soc.* *47*, 1113 (1915); *J. Chem. Soc. Abs.* *108*, 975 (1915).
[155] *Ber.* *31*, 360 (1898).

Ester	*Melting-Point*	*Boiling-Point*		*Density* 20°
Menthyl phenylacetate	......	205.5°	(25mm.)	......
Menthyl phenylproprionate ...	28.5°	216. °	(25mm.)	......
Menthyl acetoacetate	36. °	154. °	(10mm.)	......
Menthyl propyl acetoacetate ..	......	162. °	(8mm.)	......
Menthyl phenyl acetoacetate ..	69. °	131-3°	(0.1mm.)	......

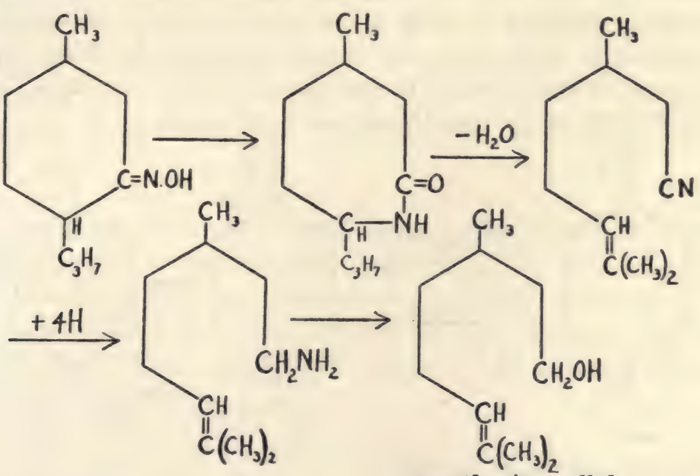
The freezing-point curves of menthyl mandelate indicate "the existence to a considerable extent, of undissociated racemate in the liquid state."[156]

Ketones of the Para-Menthane Series.

There are two saturated ketones and one known diketone derived from para-menthane.

Menthone: The stereo isomers of menthone have been discussed in connection with menthol. Ordinary menthone isolated from oil of peppermint and regenerated from the semicarbazone (melting-point 184°), boils at 208°, has a density 0.894, and refractive index 1.4496.

The oxime of menthone is of interest on account of the fact that it undergoes a Beckmann rearrangement,[157] with *rupture of the cyclohexane ring,* to give menthoneisoxime (by treating with concentrated sulfuric acid). By dehydrating agents the isoxime yields menthonitrile, which on reduction yields menthonylamine and from this amine, by heating the nitrile with water, menthocitronellol is formed, as indicated in the following outline,



menthocitronellol

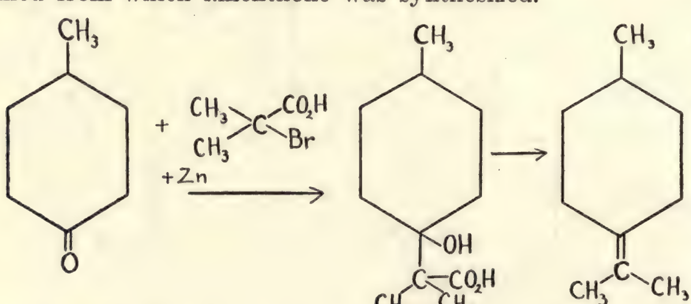
[156] Findley & Hickmans, *J. Chem. Soc. 91,* 905 (1907).
[157] Wallach, *Ann. 296,* 124.

The reduction of *l.*menthone oxime yields a single menthylamine, but by heating menthone with ammonium formate a mixture of crystalline *d.* and *l.*formylmenthylamines $C_{10}H_{19}NH.COH$ is formed, which can be separated, and which yields two isomeric menthylamines of the *cis* and *trans* types and from which a series of isomeric derivatives have been prepared.[158] When menthone oxime is heated to 220° with caustic potash[159] thymol is formed together with about 45 per cent of the open chain acid, $(CH_3)_2CH.(CH_2)_3CH(CH_3).CH_2CO_2H$.

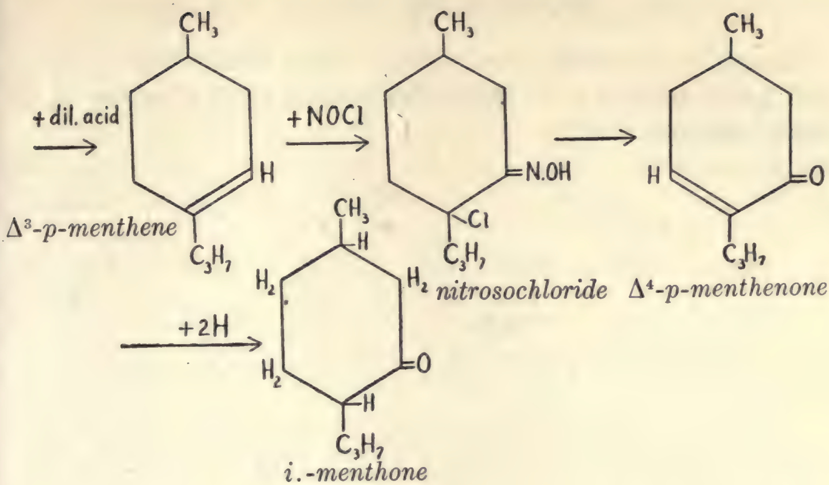
Menthone has been synthesized by Kötz[160] from β-methyl-α-isopropylpimelic acid in two ways (1) distillation of its calcium salt with soda lime, and (2), intramolecular condensation of its ester by sodium ethoxide after the manner of the acetoacetic ester condensation,

$$\begin{array}{lllll} & CH_3 & & & \\ & | & & & \\ CH_2 - & CH - & CH_2CO_2R & & \\ | & & & \\ CH_2 - & CH - & CO_2R & & \\ & | & & & \\ & C_3H_7 & & & \end{array} \longrightarrow \begin{array}{lll} & CH_3 & \\ & | & \\ CH_2 - & CH - & CH_2 \\ | & & | \\ CH_2 - & CH - & CO \\ & | & \\ & C_3H_7 & \end{array}$$

Another synthesis of menthone by Wallach and Churchill[161] is of interest. Reformatsky's reaction was employed for the condensation of 1-methylcyclohexane-4-one with α-bromoisobutyrate. The unsaturated acid, derived from the resulting ester, yields $\Delta^{4(8)}$-p-menthene. Substances containing a double bond in this position rearrange under the influence of dilute acids, the double bond shifting to the ring, as in the case of terpinolene. In the present instance i.Δ^3-p-menthene is formed from which i.menthone was synthesized.



[158] Wallach, *Ann. 343,* 67; *346,* 259.
[159] Wallach, *Ann. 389,* 185.
[160] *Ann. 357,* 209.
[161] *Ann. 360,* 26 (1908).



In a study of the chlorination and bromination of cyclic ketones Kötz [162] finds that the halogen always substitutes in an *ortho* position to the carbonyl group. In the case of menthone, 4-chloro or 4-bromo-menthane-3-one are obtained, from which aniline or aqueous potassium carbonate followed by dehydration by oxalic acid, yields Δ^4-p-menthenone. Similarly carvomenthone (p.menthane-2-one) yields 1-chloromenthane-2-one. Wallach has studied the conversion of 2.4-dibromomenthone to the *cyclopentane* hydroxy-carboxylic acid. (Cf. "Rearrangements.")

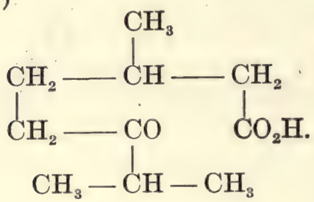
Oxidation of menthol by chromic acid [163] gives the ketonic acid $(CH_3)_2CH.CO.CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}.CH_2CO_2H$. The same acid is obtained by treating menthone with amyl nitrite and hydrochloric acid and hydrolyzing the nitrosomenthone thus formed.[164] This ketonic acid is also formed by the air oxidation of menthone, in sunlight. Sunlight in the absence of oxygen, however, decomposes menthone giving a decoic acid and an aldehyde [165] which is different from Wallach's menthocitronellaldehyde, i. e.,

[162] *Ann.* 397, 1 (1911). Kötz effects this halogenation by diluting the chlorine or bromine with air and adding water and calcium carbonate to the ketone.
[163] Beckmann, *J. Chem. Soc. Abs.* 1896 (1), 312.
[164] Baeyer & Oehler, *Ber.* 29, 27 (1896).
[165] Ciamician & Silber, *Ber.* 42, 1510 (1909).

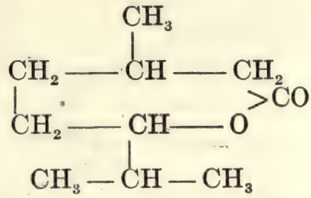
$$(CH_3)_2CH.CH\ CH.CH_2.CH(CH_3).CH_2CHO.$$[165]

Oxidation by potassium permanganate yields oxomenthylic acid (1) and β-methyladipic acid, and Caro's reagent gives a lactone of dimethyloctanolic acid (2),

(1)



(2)



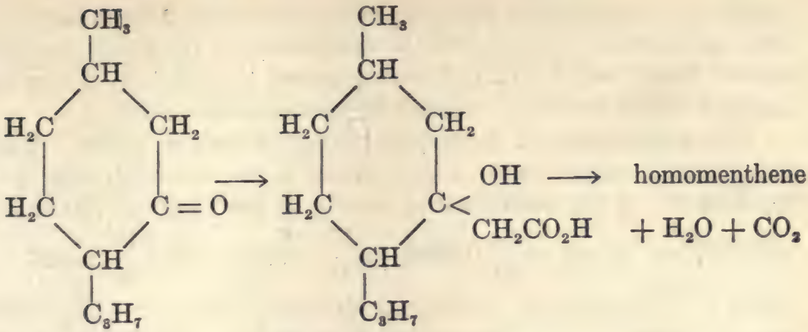
Menthone can be alkylated by Hallers' reaction[166] (sodium amide and alkyl halide), the alkyl group being substituted in position (2). One or both of the hydrogen atoms in the CH_2 group (2), can be replaced by alkyl groups.[167] With hydrazine hydrate, menthone reacts to form menthylidene hydrazine, which on heating with caustic potash loses N_2 and gives p-menthane.[168] Menthone condenses with formic acid esters (amyl formate and sodium) to form oxymethylene menthone. Benzaldehyde reacts slowly in the presence of alkalies, but rapidly with hydrochloric acid to form benzylidenementhone (hydrochloride melting at 140°). Reduction of this compound yields benzylmenthol, M.-P. 111°–112°.

Menthone,[169] like camphor, carvomenthone and cyclohexanone, acts as a catalyst in the combination of sulfur dioxide and chlorine to form SO_2Cl_2.

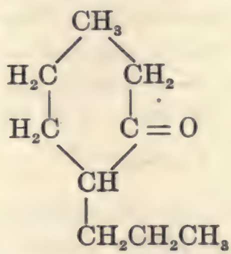
The optical inversion of *l*.menthone by sodium ethylate has been suggested as a means of determining the per cent of *l*.menthone in pine oils.[170]

Menthone reacts normally in the Reformatsky reaction,[171] with bromacetic ester and zinc, to give the ester of mentholacetic acid, the free acid readily losing water and carbon dioxide to give homomenthene $C_{11}H_{20}$, boiling at 186°–187°.

[166] Boedtker, *Bull. soc. chim.* *17*, 360 (1915).
[167] *Haller, Compt. rend.* *156*, 1199 (1913).
[168] Kizhner. *J. Russ. Phys. Chem. Soc.*, *44*, 1754 (1912).
[169] Cusmano, *Gazz. Chem. Ital.* *50* (2), 70 (1920).
[170] Gruse & Acree, *Science* *44*, 64 (1916). Tubandt [*Ann.* *377*, 284 (1910] shows that the rate of inversion of menthone by acids is not proportional to the H ion concentration. The speed of inversion is greatly retarded by water.
[171] Wallach, *Ann.* *353*, 313.



Normal Menthone, 1-methyl-4-propylcyclohexane-3-one. This ketone, synthesized by Wallach,[172] does not smell like ordinary menthone, illustrating the marked influence of slight differences of constitution on odor, noted also in the case of unsaturated ketones similar



to ionone and also in the case of artificial musk when the tertiary butyl group in Musk Bauer is replaced by similar alkyl groups. Normal menthone boils at 215°–217°.

Δ^1-p-*Menthenone,* has been found in Japanese oil of peppermint[173] and in one of the Cymbopogon grass oils, *C. senaarensis, Chiov.*[174] It boils at 235°–237°, density $\frac{19^\circ}{4^\circ}$ 0.9375, $[\alpha]_D$ 1.4875. It forms a very sparingly soluble semicarbazone melting at 212° and yields a dibromide which, by the action of aqueous caustic potash and heat, is converted almost quantitatively to thymol.

Piperitone: This menthenone occurs in the essential oils from several species of eucalyptus, particularly in *E. dives,* the oil of which contains 40 to 50 per cent of this ketone. It occurs associated with the corresponding alcohol "piperitol." As this oil is available in large

[172] *Chem. Zentr.* *1915* (2), 824.
[173] *Schimmel & Co. Semi-Ann. Rep.* *1910* (2), 79.
[174] Roberts, *J. Chem. Soc.* *1915,* 1465.

quantities it is probably only a question of a short time before menthol, and possibly thymol, will be manufactured from this material; in fact, Smith and Penfold [175] have reported that with hydrogen and catalytic nickel menthone is formed almost quantitatively.

The constitution of piperitone is not definitely known. Smith and Penfold suggest that it may prove to be identical with Δ^1-p-menthenone. They describe it as boiling at 229°–230° at 760 mm. or 106°–107° at 10 mm., $d_{20°}$ 0.9348, $[\alpha]_D$ — 40.05° and $n\frac{D}{20°}$ 1.4837. It forms a semicarbazone melting at 219°–220° and an oxime melting at 110°–111°. The most characteristic derivative is the compound formed with benzaldehyde, benzylidene *d.l.*piperitone, $C_{10}H_{14}O.CH.C_6H_5$, melting at 61°. By oxidation, by boiling with ferric chloride in dilute acetic acid, a yield of thymol corresponding to 25 per cent of the theory was obtained.

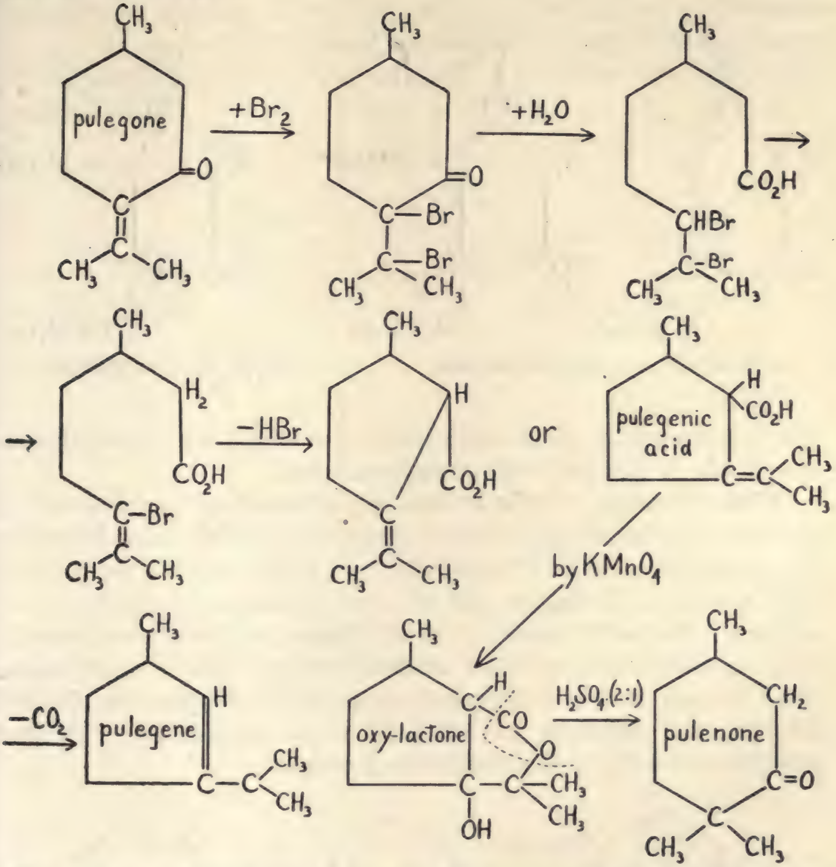
Pulegone, $\Delta^{4\cdot 8(9)}$-p-menthenone: This ketone occurs in the essential oils of *Mentha pulegium* and *Hedeoma pulegioïdes* and imparts its characteristic odor to oil of pennyroyal. Its physical properties,[176] are, boiling-point 224° (750 mm.) or 93°–94° at 869 mm., $d_{15°}$ 0.9405, $[\alpha]_D$ 20° 28′ and $n\frac{20°}{D}$ 1.48796.

By reducing energetically with nascent hydrogen [177] menthol may be obtained. When reduced by sodium and alcohol, about 30 per cent of a yellow resin, $C_{20}H_{34}O_2$, is formed,[178] a similar product being formed when employing the aluminum-mercury couple.[179] Paolini has separated the alcoholic reduction products (by sodium and alcohol) and has identified ordinary *l.*menthol of peppermint, a solid *d.*menthol melting at 88°–89°, boiling-point 214°, $[\alpha]_D$ — 11.7°, and *l.*pulegol.

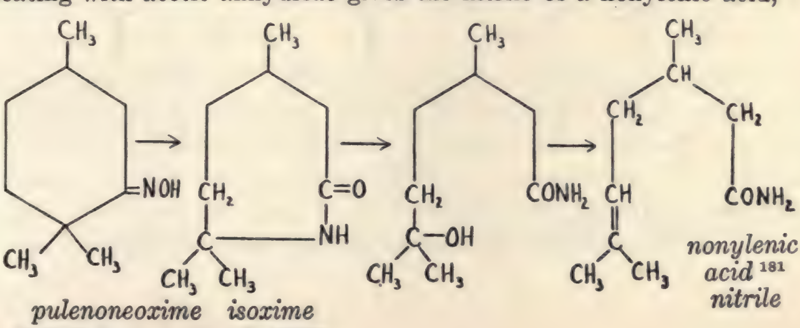
Pulegone is of special interest as furnishing an example of the conversion of the cyclohexane ring into the cyclopentane ring. When pulegone dibromide is heated with sodium methylate in alcoholic solution pulegenic acid results, and when pulegenic acid is oxidized by permanganate a glycol is formed which then forms a lactone; by a pinacoline rearrangement the cyclopentane ring is enlarged to give CO_2 (loss of 1 carbon atom) and *pulenone*, $C_9H_{15}O$.[180] Pulegenic

[175] *J. Proc. Roy. Soc. N. S. W. 54*, 40 (1920).
[176] Gildemeister, "Die Aetherischen Oele," Ed. 2, Vol. I, 463.
[177] Beckmann & Pleissner, *Ann. 262*, 30 (1891).
[178] Paolini, *J. Chem. Soc. Abs. 1920* (1), 171.
[179] Harries & Roeder, *Ber. 32*, 3357 (1899).
[180] Wallach, *Ann. 329*, 82; *376*, 154.

acid also decomposes with loss of one molecule of carbon dioxide to give pulegene, C_9H_{16}.

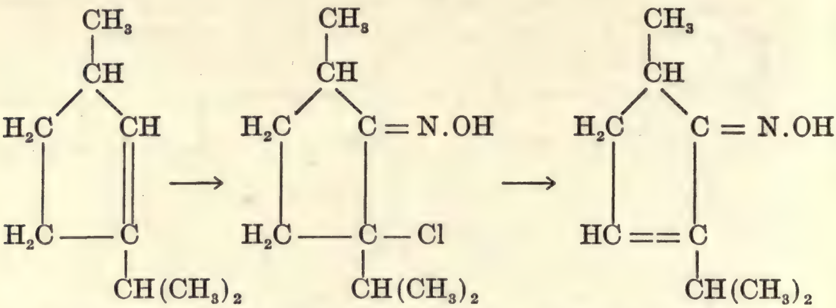


The ring in pulenone can be broken by converting the oxime into the isoxime, in the same manner as menthone, described above. Thus, heating with acetic anhydride gives the nitrile of a nonylenic acid,



[181] Wallach, *Ann.* 329, 100 (1903).

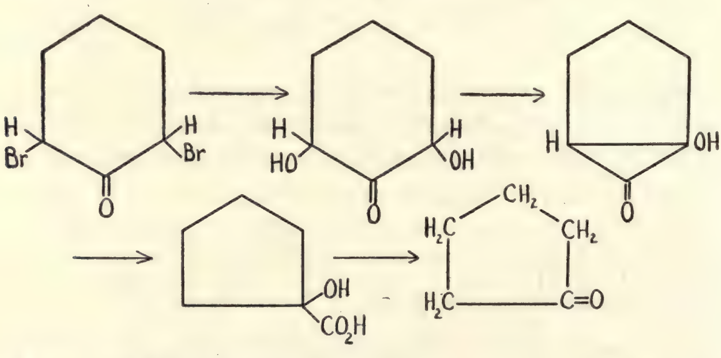
Pulegene yields a nitrosochloride, melting-point 74° to 75°, which on decomposing with alkali yields the oxime of a ketone, pulegenone,[182]



pulegene *nitrosochloride* *oxime of pulegenone*

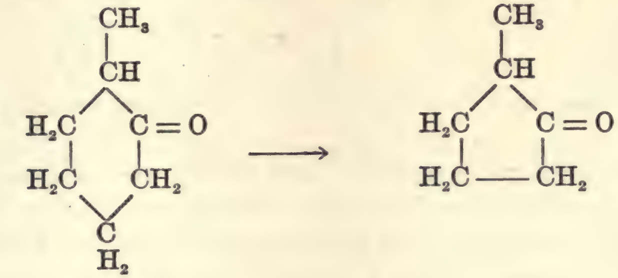
The corresponding saturated ketone, 1-methyl-3-isopropylcyclopentane-2-one, is identical with camphorphorone.

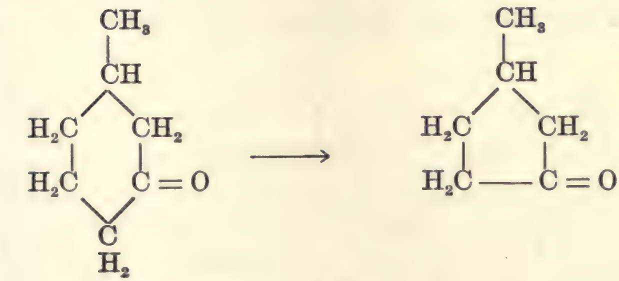
When a halogen, chlorine or bromine, is introduced into a ketone, in the ortho position to the carbonyl group, the resulting halogen derivative is unstable. Kötz[183] noted that the bromo ketones are particularly unstable, fuming in the air and decomposing rapidly when warmed. Wallach[184] showed that the dihalogen ketones react rapidly with aqueous alkali at room temperature and that cyclohexanones could be converted into cyclopentanones by evaporating the alkaline solution, thus obtaining an oxy acid which on distilling with lead peroxide and sulfuric acid yields the pentanone,

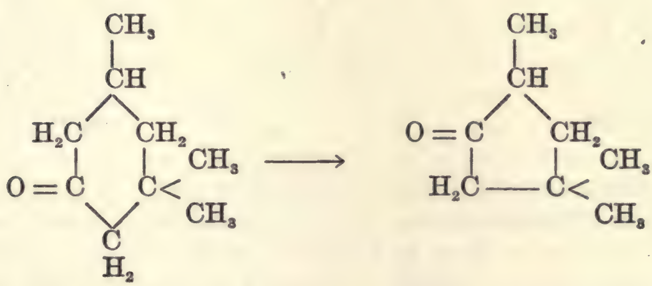


[182] Wallach. *Ann.* *327*, 133 (1903).
[183] *Ann.* *400*, 47 (1913).
[184] *Nachr. Goettingen 1915*, 244; *J. Chem. Soc. Abs.* *110* (1), 487 (1916).

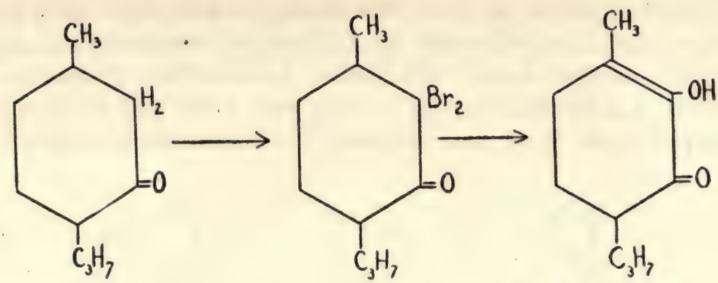
By a similar series of reactions methylcyclohexane-2-one gives 1-methycyclopentane-2-one; 1-methylcyclohexane-3-one gives 1-methycyclopentane-3-one; the ketone 1.3-dimethylcyclohexane-5-one yields 1.3-dimethylcyclopentane-2-one; from 1.3.3-trimethylcyclohexane-5-one there was obtained 1.3.3-trimethylcyclopentane-5-one.







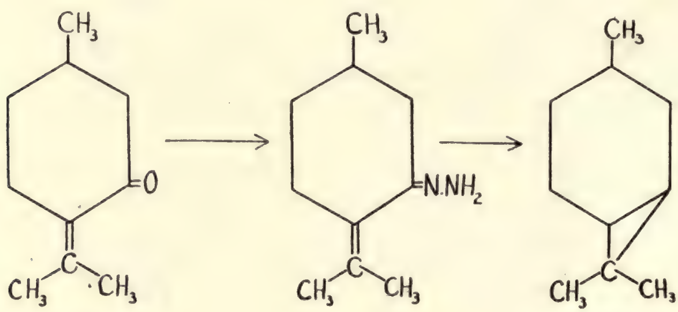
Menthone similarly gives 1-methyl-3-isopropylcyclopentane-2-one (dihydrocamphorphorone), and carvomenthone gives the same oxidation products. Menthone can also be converted into pulegenone by slightly modifying the above procedure. Wallach finds that menthone dibromide first yields two isomeric substances $C_{10}H_{16}O_2$, one of which proved to be buchu camphor.



menthone *buchu camphor*

The dibromide of buchu camphor, when treated with aqueous alkali, gives an oxy-acid which on distillation yields pulegenone.[185]

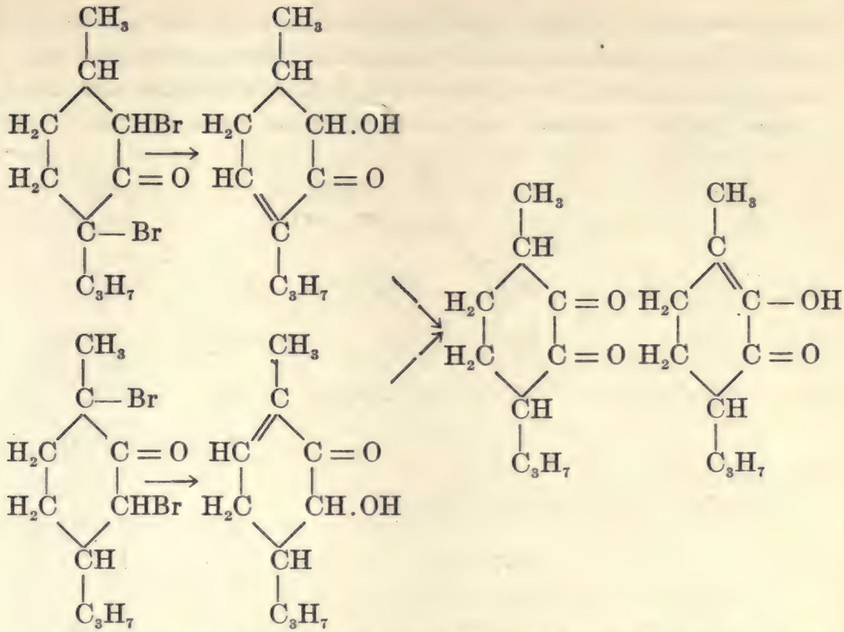
The hydrazine derivative of menthone yields para-menthane when heated with caustic potash. Pulegohydrazine, however, yields the bicyclic hydrocarbon carane, under these conditions.[186]



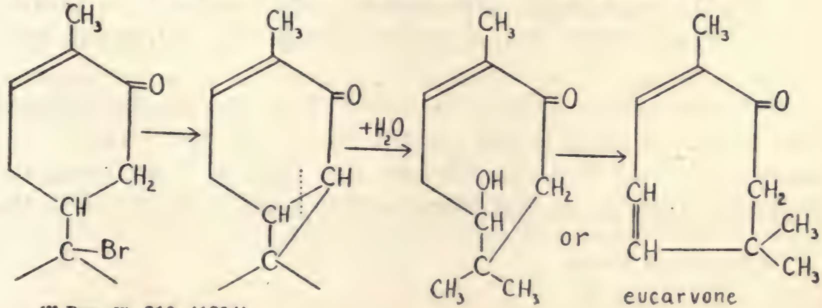
pulegone *carane*

This substance, also called diosphenol, is found in nature in the essential oil of buchu leaves. It is of considerable interest in that its chemical behavior gives no indication of the existence of the tautomeric diketo form, analogous to camphor quinone, although its formation from the dibromine substitution products of *both* menthone and carvomenthone indicate that the diketone must be an intermediate product.[187]

[185] Wallach, *J. Chem. Soc. Abs. 114*, 544 (1918).
[186] Kizhner. *J. Russ. Phys.-Chem. Soc., 43*, 1132 (1911).
[187] Cusmano, *J. Chem. Soc. Abs. 1914* (1), 303; *Atti accad. Lincei* (5), *24*, 520 (1915).

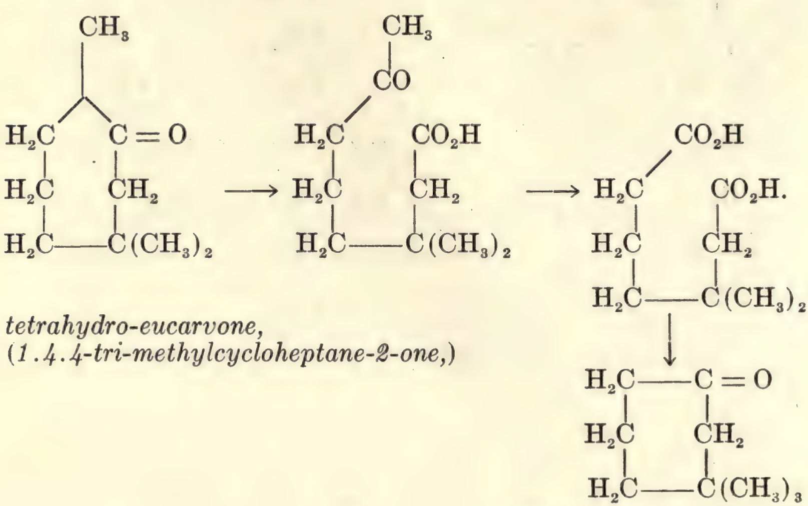


Carvone, $\Delta^{6\cdot 8(9)}$-p-menthadiene-2-one. The constitution of carvone and much of the chemical behavior has been shown above, in connection with the discussion of limonene and the terpineols. Carvone is of further interest, however, on account of its conversion to the cylcoheptane derivative *eucarvone,* and derivatives of the bicyclic *carane* series. Baeyer [188] showed that the hydrobromide of carvone gave, by loss of HBr, an isomeric ketone which he called eucarvone. Baeyer originally suggested that the constitution of eucarvone was that represented as I, below, but Wallach was able to show that eucarvone is a cycloheptane derivative II, and that Baeyer's structure for eucarvone is in fact possessed by an intermediate product in the reaction. Wallach [189] represents these reactions as follows,



[188] *Ber.* **27**, 810 (1894).
[189] *Ann.* **339**, 94.

Baeyer regarded dihydro and tetrahydroeucarvone as cycloheptane derivatives and showed that the completely reduced tetrahydroeucarvone was broken up by oxidation to β, β-dimethylpimelic acid which in turn yields 1.1-dimethylhexane-3-one, in the usual manner:



tetrahydro-eucarvone,
(1.4.4-tri-methylcycloheptane-2-one,)

dimethylcyclohexanone

Eucarvone boils at 85°–87° (12 mm.); its density at 21° is 0.949 and $n\frac{20°}{D}$ 1.5048. It yields a semicarbazone melting at 183°–185° and a benzylidene derivative melting at 112°–113°. The oxime melting-point, 106°, may be reduced by sodium and alcohol to dihydroeucarvylamine and, by more energetic reduction, to the saturated amine $C_{10}H_{19}.NH_2$. Reduction of the oxime by hydrogen and palladium yields the dihydro and tetrahydrooximes, melting at 122°–123° and 56°–57° respectively. The alcohol, tetrahydroeucarveol [1.4.4-trimethylcycloheptanol(2)], a product of reduction by sodium, boils at 216°.

When carvone is reduced by nascent hydrogen the double bond next to the CO group is first reduced, dihydrocarvone being $\Delta^{8(9)}$-p-menthene-2-one. Wallach, Albright and Klein[190] have made the interesting observation that when the CO group is converted to the

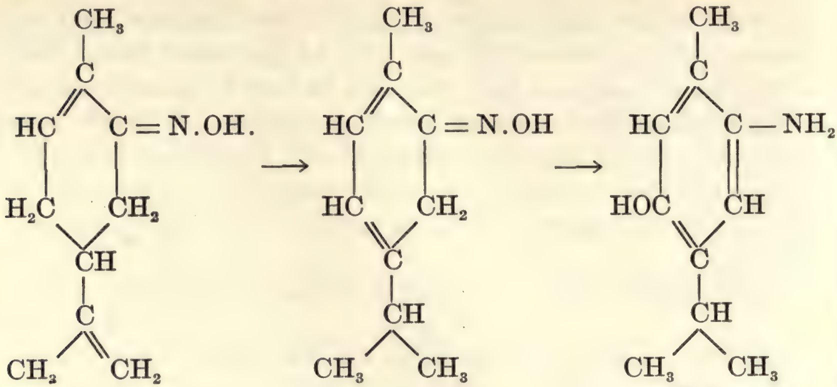
[190] *Ann.* 403, 74 (1914).

oxime and the resulting carvoxime then reduced by one mole of hydrogen, in the presence of Paal's colloidal palladium, the double bond in the side chain is first reduced. In this case the oxime of carvotanacetone (Δ^6-p-menthene-2-one) is formed. Vavon[191] also showed that, in the presence of platinum black (Willstätter's method), carvone itself was reduced first to carvotanacetone. This ketone is also formed by the rupture of the three carbon ring in thujone, effected by heating.[192]

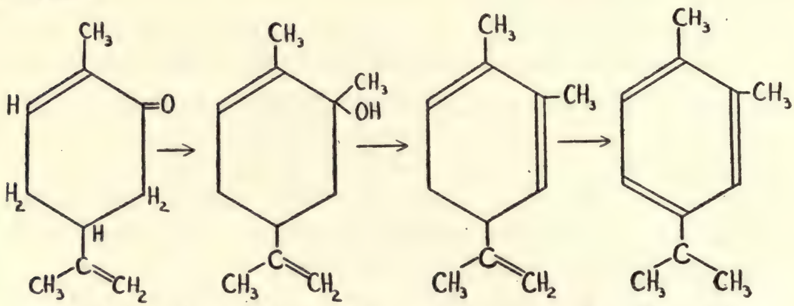
Carvone boils at 230° and occurs in *d.* and *l.* forms $[\alpha]_D \pm 60°$ Carvone, dihydrocarveol and limonene are the principal constituents of oil of caraway, used in making the liqueur "kümmel"; carvone is also an important constituent of dill and spearmint oils. Like citral and other substances containing the group $-CH=CH-CO-$ carvone reacts to form an unstable bisulfite compound from which carvone can be regenerated by alkali, and also forms stable salts of the dihydrosulfonic acid derivative, from which the ketone cannot be regenerated. Carvone forms a crystalline compound with hydrogen sulfide, $(C_{10}H_{14}O)_2.H_2S$, from which carvone can be regenerated.[193] The bisulfite method is preferable for the isolation of carvone. For its identification, the following derivatives are characteristic: the *d.* and *l.*oxime, melting-point 72°, i-carvoxime melting-point 93° (when too great an excess of hydroxyamine is employed a compound of carvoxime and hydroxylamine, $C_{10}H_{14}NOH.NH_2OH.$, melting at 174°–175°, is formed. It will be of interest to note that in the preparation of carvoxime a Walden inversion occurs, *d.* carvone yielding *l.*carvoxime and *l.*carvone yielding *d.*carvoxime. With phenylhydrazine carvone forms a phenylhydrazone melting at 109°–110° and semicarbazid forms a semicarbazone melting at 162°–163° in the case of *d.* or *l.*carvone but i-carvone yields the racemic semicarbazone melting at 154°–156°. The original ketones are readily regenerated by warming the semicarbazones with oxalic acid.

Carvoxime rearranges to amido thymol when treated with concentrated sulfuric acid,

[191] *Compt. rend.* *153,* 68 (1911).
[192] Semmler, *Ber.* *27,* 895 (1894).
[193] Wallach, *Ann.* *305,* 224 (1889) ; Claus & Fahrion, *J. prakt. Chem.* (2), *39,* 365 (1889). The product from *d.* or *l.* carvone melts at 210°-211° ; that from *i.* carvone melts at 189°-190°. It is dimolecular in benzene but monomolecular in glacial acetic acid. Deussen, *Arch. Pharm.* *221,* 285 (1883).



By the Grignard reaction, using methyl-magnesium iodide, a hydrocarbon, $C_{11}H_{16}$, results.[194] Klages regards this hydrocarbon as 2-methyl-$\Delta^{2,6,8(9)}$-menthatriene on account of the ease with which it is isomerized to 2-methylcymene by boiling with a 2 per cent solution of hydrogen chloride in acetic acid.[195] The reaction is worth noting as one of the many instances of the migration of a double bond from a side chain to the cyclohexadiene nucleus to give a benzene derivative.



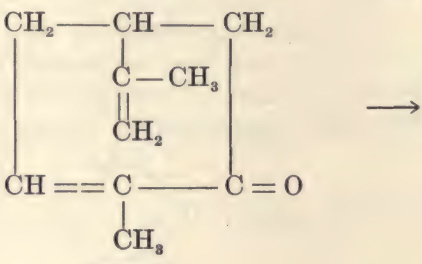
When dihydrocarvone is similarly treated, 2-methyldihydrocarveol results which can be decomposed directly, or better by converting to the corresponding chloride, to 2-methylhomolimonene, or hydrated by the action of alcoholic sulfuric acid to 2,8-dihydroxy-2-methylmenthane.[196] The main product of the action of magnesium-benzyl-

[194] Rupe & Liechtenhan, *Ber.* *39*, 1119 (1906).
[195] *Ber. 39*, 2306 (1906); Rupe & Emmerich, *Ber.* *41*, 1393 (1908).
[196] Rupe & Emmerich, *loc. cit.*

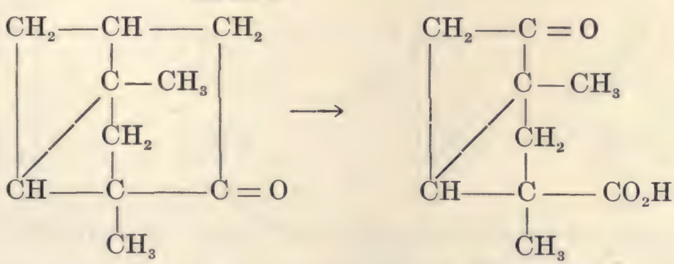
chloride is a ketone, 6-benzyl-Δ^8-p-menthene-2-one, [or 6-benzyldihydrocarvone], melting at 73°. The α-naphthyldihydrocarvone, melting-point 150°, was prepared in the same manner.[197]

Semmler [198] has employed the reaction of carvone with magnesium-isoamylbromide for the synthesis of a hydrocarbon of the sesquiterpene class. (When ether is used as a solvent in the Grignard reaction, instead of benzene, a large proportion of isoamyldihydrocarvone is formed.) The synthetic sesquiterpene thus prepared is monocyclic, contains three double bonds and has been named isoamyl-α-dehydrophellandrene by Semmler.

Carvone is isomerized by sunlight forming a resin and a crystalline camphor-like substance, melting at 100°, which Ciamician and Silber named carvone-camphor.[199] This substance has been carefully investigated by Sernagiotto,[200] who showed that, in sealed tubes, the sunlight causes both double bonds in carvone to combine to form a four-carbon ring. Ciamician had suggested that the isomerization of carvone resembled that of the condensation of two molecules of cinnamic acid to form truxillic acid. The work of Sernagiotto shows that the chemical behavior of the substance may be indicated as follows,



carvone



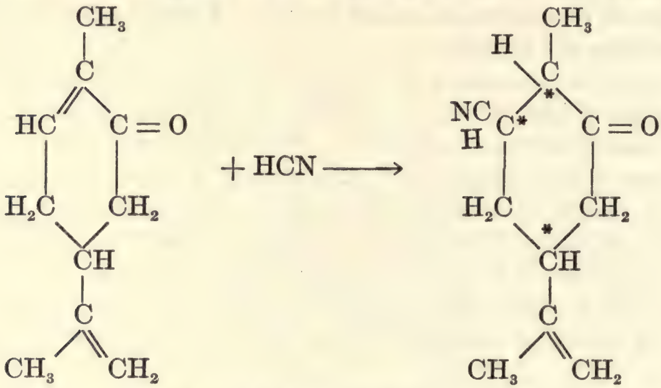
carvone-camphor *ketonic acid*

[197] Rupe & Tomi, *Ber.* *47*, 3064 (1914); Zelinski, German Pat. 202,720 (1909).
[198] *Ber.* *50*, 1838 (1917).
[199] *Ber.* *41*, 1928 (1908).
[200] *Atti accad. Lincei* *23* (2), 70 (1914); *26*; 238 (1917).

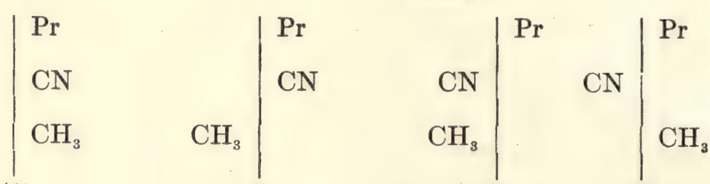
Carvone camphor melts at 100°, boils at 205.5°, forms an oxime melting at 126°–128° and a semicarbazone melting at 239°.

Like menthone, pulegone and camphor, carvone can be condensed with aniline by heating with aniline in the presence of a little zinc chloride [or $ZnCl_2 . (C_6H_5NH_2)_2$]. The resulting carvoneanil is an oil.[201]

It is pointed out by Lapworth [202] that when the double bond in the ring of carvone combines with hydrogen cyanide, the resulting



cyanodihydrocarvone should theoretically be capable of existence in four stereoisomeric forms having three asymmetric carbons, as shown. By employing Aschan's scheme of representing the section of the ring plane by a line, these four isomerides can be represented as follows, Pr representing the group $-\mathrm{C}\begin{array}{l}/\mathrm{CH_3}\\ \backslash\backslash\,\mathrm{CH_2}\end{array}$



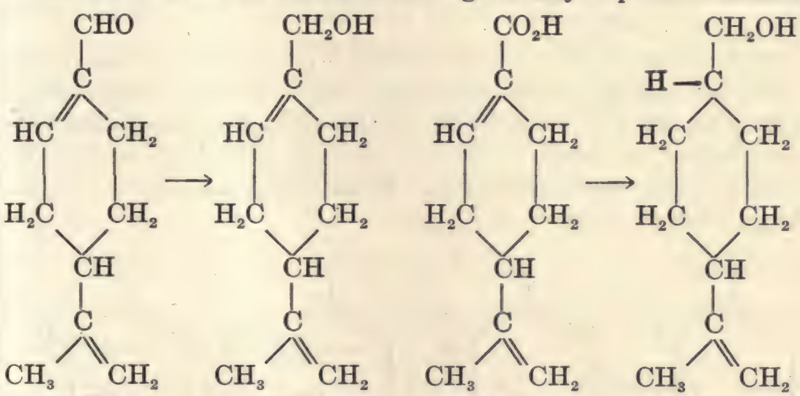
(1) (2) (3) (4)

The ordinary form, melting-point 93.5°–94.5°, is obtained in excellent yields when an alcoholic solution of carvone and potassium cyanide is treated with acetic acid in amounts which insure the presence of a

[201] Reddelien & Meyn, *Ber.* 53, *B.* 345 (1920).
[202] *J. Chem. Soc.* 89, 946 (1906).

little excess potassium cyanide. When the addition of hydrogen cyanide takes place in hot solutions a different crystalline isomeride is produced in considerable quantity which has a rotatory power in the opposite sense to that of the substance described above $[\alpha]_D$ —39°, instead of $[\alpha]_D$ + 15.4°. The *l*.isomeride exhibits slight mutarotation and Lapworth considers that the four isomerides may be divided into two pairs, the two members of each pair being dynamic isomerides at ordinary temperatures.[203]

Perillic aldehyde, occurring in the essential oil of *Perilla nankinensis,* has been found to contain two double bonds in the $\Delta^{6,8(9)}$ positions, as in limonene. By reduction with zinc dust and acetic acid an alcohol is produced which is identical with the so-called dihydrocuminic alcohol previously found in gingergrass oil. Its constitution was shown by converting the CH_2OH group of perillic alcohol to the chloride which on reducing by sodium and alcohol gave *l*.limonene. On dehydrating the oxime of perillic aldehyde the corresponding nitrile is formed which on hydrolysis yields perillic acid. Reduction of the ester of perillic acid with sodium in absolute alcohol reduced one of the double bonds and gave dihydroperillic alcohol.[204]



perillic aldehyde [265] *perillic alcohol* *perillic acid* *dihydroperillic alcohol*

[203] Lapworth & Steel, *J. Chem. Soc. 99,* 1877 (1911).
[204] Semmler & Zaar, *Ber. 44,* 52 (1911).
[205] The physical properties of these substances are as follows:

	Perillic aldehyde	*Perillic alcohol*	*Perillic nitrile*	*Perillic acid*
Boiling-point (10mm.) ..	104°-105°	119°-121° (11mm.)	116° (11mm)	164°
Density	0.9617 (18°)	0.9640 (20°)	0.9439	——
[α] D	—146°	—68.5°	—115°	—20° (25% alcohol)
nD	1.5074	1.4996	1.4977	——

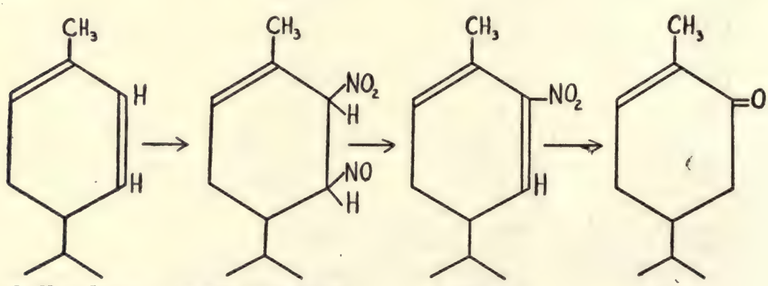
Perillic acid melts at 130°-131°.

The Phellandrenes.

As early as 1842, Cahours noted a terpene boiling at 173°–175° in the essential oil of bitter fennel, which gave a crystalline nitrosite. The correct empirical formula of this nitrosite, $C_{10}H_{16}N_2O_3$, was first established by Pesci,[206] who showed that "phellandrene" from the essential oil of water fennel, *Phellandrium acquaticum*, also yielded a nitrosite of the same empirical formula. Both phellandrenes were dextro-rotatory and yielded lævo nitrosites of nearly identical physical properties; the phellandrenes from both sources were unstable and even by repeated distillation were converted to limonene. Wallach took up the study of the phellandrenes in 1902 and a little later [207] showed that *d*.phellandrene from elemi oil and *d*.phellandrene from bitter fennel oil were identical in every respect and that *l*.phellandrene from *Eucalyptus amygdalina* oil was the corresponding lævo form; that the *d*.phellandrene from water fennel oil is a different hydrocarbon, and therefore designated the two hydrocarbons as α-phellandrene and β-phellandrene, respectively.

That α-phellandrene belonged to the paramenthane series of hydrocarbons was early recognized by reason of the easy conversion of the dibromide to cymene.[208]

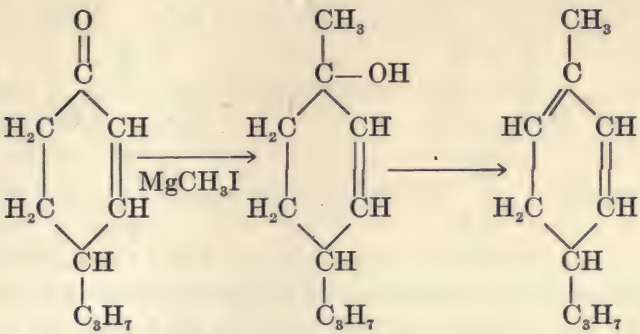
The constitution [209] of α-phellandrene is indicated by its conversion to carvotanacetone (Δ^6-p-menthene-2-one). When α-phellandrene nitrite is heated with alcoholic caustic potash, nitro-α-phellandrene is formed which, on careful reduction by zinc and acetic acid, yields carvotanacetone, the constitution of which had previously been established,



α-phellandrene *α-phellandrene nitrite* *nitro-α-phellandrene* *carvo-tanacetone*

[206] *Gazz. chim. Ital. 16,* 225 (1886).
[207] *Ann. 336,* 9 (1904).
[208] *Ann. 287,* 383.
[209] Wallach, *loc. cit.*

The constitution of α-phellandrene shown above is confirmed by its synthesis from 4-isopropyl-Δ^2-cyclohexenone.[210]

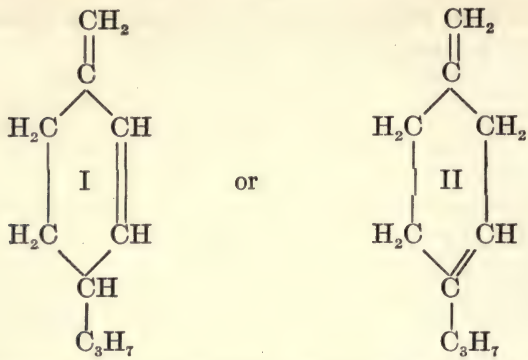


In carrying out the above synthesis the intermediate alcohol is not liberated as such but the magnesium-methyl halide addition product decomposes in the reaction mixture to give the hydrocarbon. Hydrocarbon formation is often observed under these conditions.

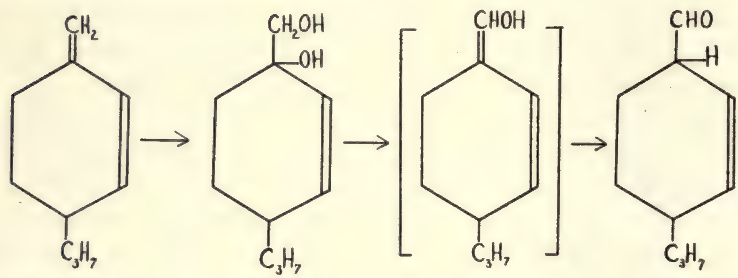
α-Phellandrene nitrite is known in two forms. It is best prepared[211] in ligroin solution, shaking the ligroin-phellandrene mixture with concentrated aqueous sodium nitrite acidified by acetic acid. The two nitrites may be separated by crystallization from dilute acetone. The sparingly soluble α-nitrite, melts at 112°–113°, $[\alpha]_D + 136°$ to $143°$, $[\alpha]_D - 138°$. The β-nitrite is more soluble and melts at 105° $[\alpha]_D + 45.8°$ and $[\alpha]_D - 40.8°$. On reduction these nitrites give a diamine, the hydrochloride of which decomposes on distillation yielding cymene.

β-Phellandrene also yields two known nitrites, the so-called α-nitrite melting at 102° and the β-nitrite melting at 97°–98°. When β-phellandrene nitrite is converted to nitro-β-phellandrene and when this is reduced by sodium and alcohol, dihydrocumin aldehyde is produced,[212] indicating that its structure is either

[210] Wallach, *Ann.* *359,* 285.
[211] Wallach, *Ann.* *313,* 345 ; *336,* 13.
[212] Wallach, *Ann.* *340,* 9.

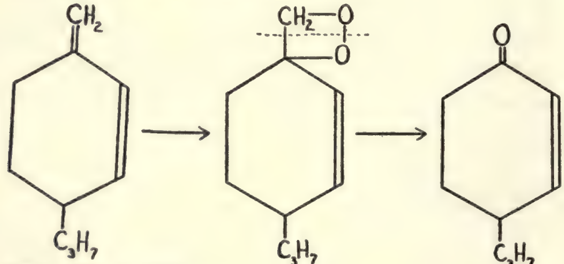


However, β-phellandrene is optically active which eliminates II, which has no asymmetric carbon atom. The decomposition of nitro derivatives with the formation of aldehydes has been observed by Konowalow[213] and others. Careful oxidation of β-phellandrene by permanganate yields first a glycol which on decomposing with acids, yields tetrahydrocuminaldehyde,



β-phellandrene *glycol* *tetrahydrocuminaldehyde*

Isopropylcyclohexenone is formed by air oxidation of β-phellandrene in the presence of moisture,[214] which may be expressed, according to Engler's theory of air oxidation, as follows,



[213] *Chem. Zentr. 1889,* I, 1238.
[214] Wallach, *Ann. 343,* 29 (1905).

The following physical properties of the phellandrenes have been noted:

l.α-phellandrene, boiling-point 65° (12mm.), $d_{19°}$ 0.8465, n_D 1.488.

d.α-phellandrene, boiling-point 61° (11mm.), $d_{19°}$ 0.844, n_D 1.4732.

Synthetic α-phellandrene, boiling-point 175°–176° $d_{22°}$ 0.841, n_D 1.4760, M_D 45.61.

d.β-phellandrene, boiling-point 57° (11mm.), $d_{20°}$ 0.8520, $n_D^{20°}$ 1.4788, $[\alpha]_D + 18.54$ (?).

The essential oil of *Bupleurum fruticosum* yields *d*.β-phellandrene showing an optical rotation of $[\alpha]_D$ 65.2°, from which fact, together with evidence obtained by a study of the oxidation products and the nitrosochlorides, the discoverers [215] conclude that the *d*.β-phellandrene of Pesci and Wallach, which showed a much lower rotatory value, is a mixture of the two optical antipodes. A terpene fraction boiling at 169°–171°, isolated [216] from the volatile oil of *Rubieva multifida* of California, and consisting "largely" of β-phellandrene, showed $[\alpha]_D + 46.4°$.

Hydrogen chloride passed into an alcoholic solution of β-phellandrene gives α-terpinene dihydrochloride.[217]

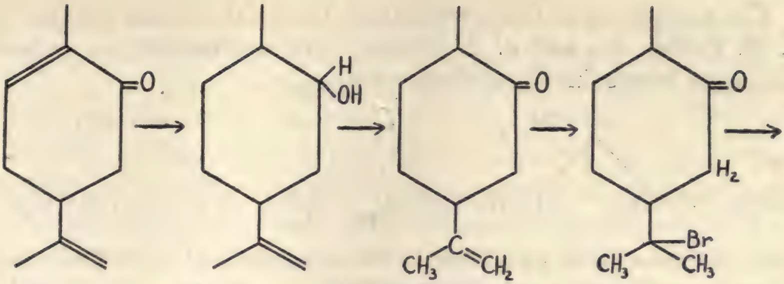
[215] Fransesconi & Sernagiotto, *Gazz. chim. Ital.* 46 (1), 119 (1916).
[216] Nelson, *J. Am. Chem. Soc.* 42, 1286 (1920).
[217] Fransesconi & Sernagiotto, *Gazz. chim. Ital.* 44 (2), 456 (1914).

Chapter X. Cyclic Non-benzenoid Hydrocarbons.

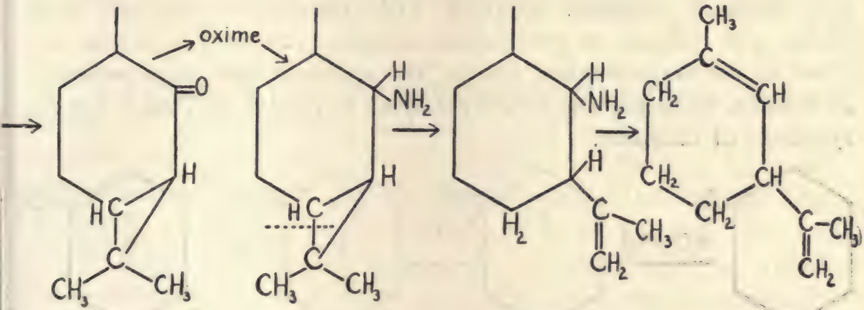
Ortho- and Meta-Menthanes and Their Derivatives.

Sylvestrene: The most important derivative of this series is sylvestrene, a terpene discovered by Atterberg in Swedish oil of turpentine, from *Pinus sylvestris*. Its physical properties are nearly identical with those of limonene, boiling at 175°–176°. It is one of the most stable of the terpenes and is not isomerized to other terpene hydrocarbons either by the action of heat or dilute acids. Its relation to meta-cymene was shown by Baeyer by first reacting upon it by hydrogen bromide forming the dihydrobromide (melting-point 72°), introducing a third bromine atom and treating the tribromide with zinc dust and alcoholic hydrochloric acid when *meta*-cymene was produced. Under these same condition limonene gives *para*-cymene. The inactive form of this terpene has been called *carvestrene* and bears the same relation to sylvestrene that dipentene bears to limonene. Baeyer[1] made i-sylvestrene from carvone by reducing this ketone by sodium and alcohol to dihydrocarveol, oxidizing this alcohol to dihydrocarvone and adding hydrogen bromide to the latter ketone; when the hydrobromide of dihydrocarvone is treated with cold alcoholic caustic potash, *carone* is formed, which substance has been shown to have a cyclopropane ring. The oxime of carone is reduced in the usual manner to the corresponding amine, and warming with dilute acids ruptures the three-carbon ring. When the hydrochloride of this amine is heated, ammonium chloride is split off and i-sylvestrene (carvestrene) is produced.

[1] *Ber.* 27, 3485.



carvone *dihydrocarveol* *dihydrocarvone*



carone *vestrylamine* *i-sylvestrene*

The nature of the reaction taking place when the hydrobromide of dihydrocarvone is treated with alkali to form carone, and the constitution of carone, was first suggested by Wagner, whose views were accepted by Baeyer. In conjunction with Ipatiev, Baeyer investigated the oxidation of carone by permanganate [2] and showed the formation of two isomeric dibasic acids, $C_5H_8(CO_2H)_2$, one of which readily forms an anhydride (when boiled with acetyl chloride) but the other does not form an anhydride under these conditions. Their research led Baeyer and Ipatiev to the conclusion that these two *caronic acids* were *cis* and *trans* modifications of the following structure,

$$\begin{array}{ccccc} & & C(CH_3)_2 & & \\ & \diagup & & \diagdown & \\ HO_2C - & C & \text{——} & C & - CO_2H \\ & | & & | & \\ & H & & H & \end{array}$$

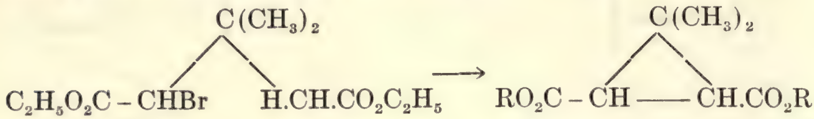
trans-caronic acid

$$\begin{array}{ccccc} & & C(CH_3)_2 & & \\ & \diagup & & \diagdown & \\ H - & C & \text{——} & C & - H \\ & | & & | & \\ & CO_2H & & CO_2H & \end{array}$$

cis-caronic acid

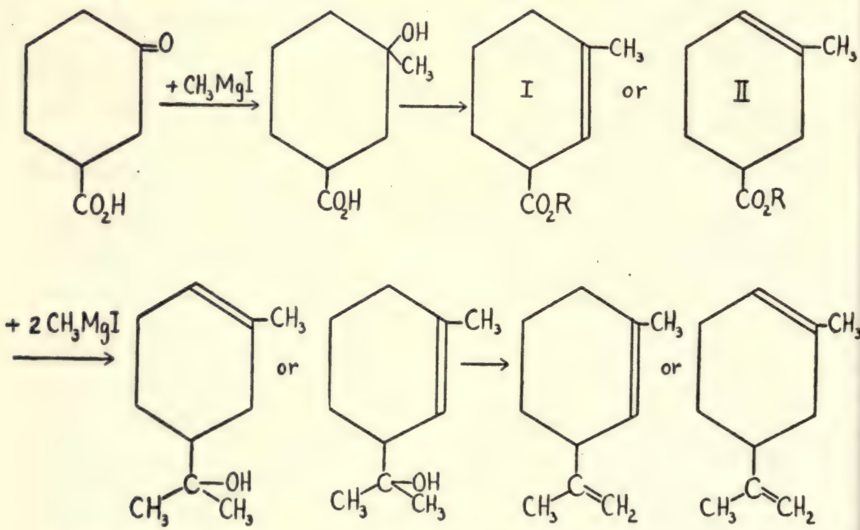
[2] *Ber.* **29**, 2796 (1896).

The correctness of the constitutions shown above was proven by W. H. Perkin, Jr., and J. F. Thorpe,[3] who synthesized the caronic acids from bromodimethylglutaric ester,



Trans-caronic acid is converted to the anhydride of *cis*-caronic acid by heating with acetic anhydride at 220°.

Inactive sylvestrene has been synthesized by Perkin[4] by means of the Grignard reaction. Starting with meta-hydroxybenzoic acid, which was reduced to cyclohexanol-3-carboxylic acid and this oxidized to the corresponding ketone, the reactions may be represented as follows, being parallel to the reactions employed by Perkin for the synthesis of limonene.



It is evident that Baeyer's i-sylvestrene can be only the Δ^1 hydrocarbon, but Perkin's synthetic hydrocarbon may, from the method of its preparation, be either Δ^1 or Δ^6 hydrocarbon, although Perkin's results indicate that his synthetic sylvestrene consists at least mainly of the Δ^1 product.

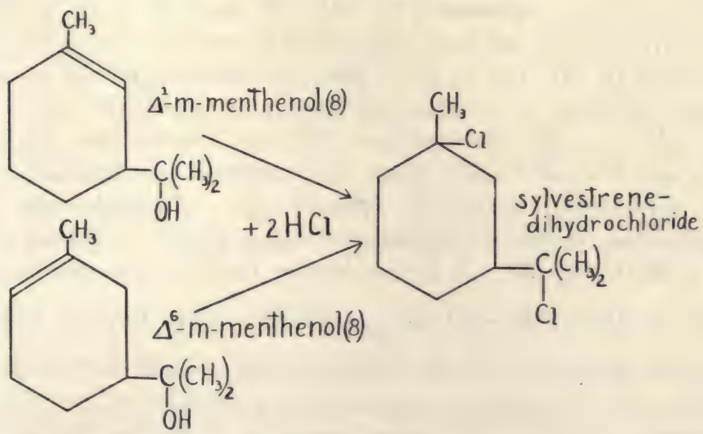
[3] *J. Chem. Soc. 75*, 49 (1899).

[4] *J. Chem. Soc. 91*, 482 (1907). It was believed at the time that the unsaturated acid was II, but later work (*J. Chem. Soc. 103*, 2227 [1913]), showed that the product is a mixture of the two acids I and II.

Sylvestrene cannot be isolated from Swedish oil of turpentine by fractional distillation on account of the presence of other terpenes of practically the same boiling point. It has usually been prepared by making the crystalline dihydrochloride from the fraction boiling at 173°–178° and decomposing this with an alkali or an organic base. Wallach observed that the terpene so prepared was not pure but by fractional distillation of the product obtained by decomposition of the dihydrochloride obtained a sylvestrene of the following physical properties.

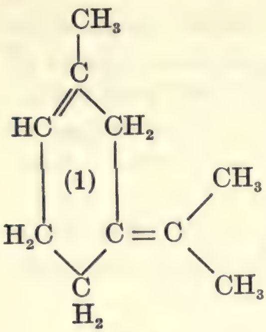
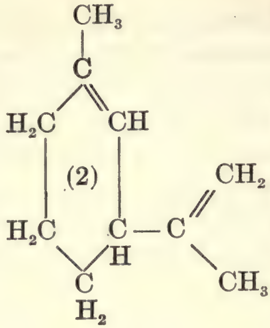
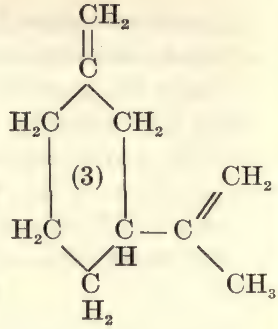
Blg.-pt. 175°–176°; $d_{20°}$ 0.848; n_D 1.4757; $[\alpha]_D$ + 66.32.

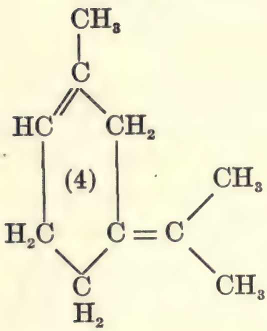
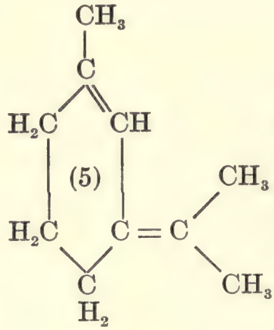
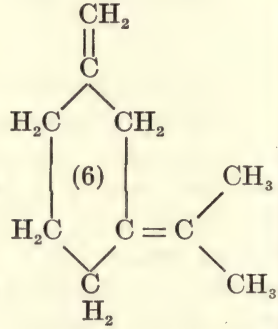
It is well known that the decomposition of dipentene dihydrochloride or ordinary terpin, and also terpinene dihydrochloride or terpinene-terpin (1.4 terpin) yields mixtures of terpenes and it would therefore appear probable that the decomposition of sylvestrene dihydrochloride would also yield a mixture of hydrocarbons. The first definite demonstration that sylvestrene dihydrochloride is 1.8-dichloro-m.-menthane was the conversion of *dl.-m.-Δ¹-menthenol*(8) and *dl.-m.*-Δ⁶-menthenol(8) into this dihydrochloride,[5]



The decomposition of this dihydrochloride could possibly yield the following six isomeric meta-menthadienes.

[5] Perkin & Tattersall, *J. Chem. Soc. 91*, 481 (1907); Perkin & Fisher, *ibid., 93*, 1888 (1908).

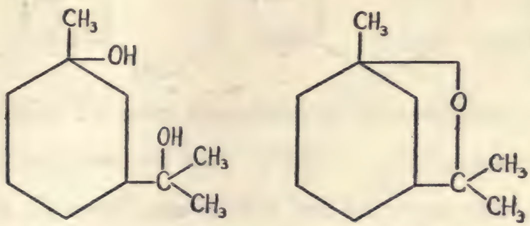




The hydrocarbons represented by (4), (5), and (6) have no asymmetric carbon atom and since sylvestrene is optically active its structure cannot be (4), (5) or (6). Also, sylvestrene does not show the chemical behavior of a substance having a semicyclic $>C=CH_2$ group, which renders the structure (3) very improbable. Haworth, Perkin and Wallach [6] have shown that repeated fractionation of the crude sylvestrene, made by heating the dihydrochloride with diethylaniline, yields a sylvestrene boiling at 175° (751mm.) and $[\alpha]_D + 83.18°$ at 18°. A higher boiling fraction was also isolated, boiling at 182°–184° and $[\alpha]_D + 45.42°$. This terpene resinifies rapidly on exposure to air, or in contact with sodium, and the authors conclude that it contains a considerable proportion of inactive sylveterpinolene together with some isomeride of similar boiling-point but optically active. The purest sylvestrene thus obtained, boiling at 175°, is regarded as a mixture of the Δ^1 and Δ^6 isomerides, (1) and (2) above. All efforts to obtain a pure sylvestrene of definite con-

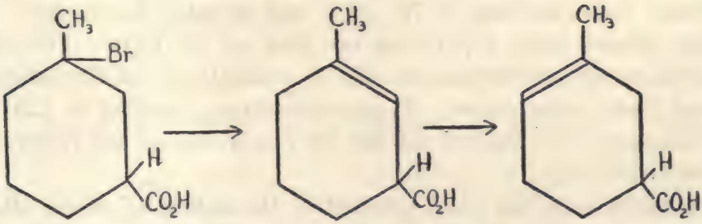
[6] *J. Chem. Soc.* 103, 1230 (1913).

stitution by the dehydration of sylveterpin, under different conditions, were without success owing to the marked tendency of the sylveterpin to form meta-cineol,



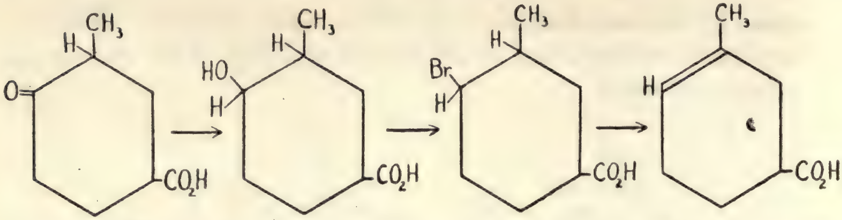
The complexity of the problem is indicated in the foregoing discussion but, nevertheless, Haworth and Perkin[7] were able to synthesize both optically active forms of sylvestrene and their research, culminating with the synthesis of *d.* and *l.*sylvestrene, is one of the most interesting examples of refined experimental method and application of the theories of organic chemistry.

The removal of hydrogen bromide from 1-bromo-1-methylcyclohexane-3-carboxylic acid yields a mixture of the Δ^1 and Δ^6 unsaturated acids.



By fractional crystallization of the brucine salt an optically active acid $[\alpha]_D + 108°$ was isolated, and from the mother liquors, by employing *l.*menthylamine, another acid $[\alpha]_D - 49.7°$ was obtained. In order to show which of these acids was the Δ^1 and which the Δ^6 acid, the latter was synthesized from 1-methylcyclohexane-6-one-3-carboxylic acid,

[7] *J. Chem. Soc.* **103**, 2229 (1913).



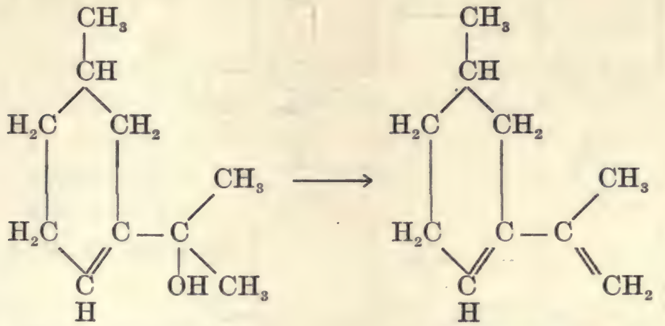
and this, on resolution by brucine, also gave an acid $[\alpha]_D + 108°$ and the lævo form $[\alpha]_D - 98.6°$. This dextro-rotatory acid, from both sources, was converted into d-Δ^6-m-menthenol(8), which in turn was changed to *d.-sylvestrene dihydrochloride*, $[\alpha]_D + 22.5°$, which on decomposition by diethylaniline gave *d-sylvestrene*, $[\alpha]_D + 67.5°$. The lævo Δ^6 acid, $[\alpha]_D - 98.6°$, and the lævo Δ^1 acid, $[\alpha]_D - 49.7°$ both gave *l-sylvestrene*, by similar reactions, the rotation being — 66.5° in one case and — 68.2° in the other.

Sylveterpin and Sylveterpineols: When sylvestrene dihydrochloride is shaken with dilute aqueous caustic potash the corresponding terpin is formed. Like ordinary terpin, sylveterpin exists in two modifications of the *cis* and *trans* type, the *cis* form melting at 137°–138°, being less soluble, was discovered first,[8] and the more soluble *trans* form, melting at 70°–75°, was recently discovered [9] in the mother liquors after separating the first or *cis* form. The *cis* and *trans* forms of sylveterpin are the *d.* constituents of the inactive or *cis* and *trans carveterpins. Trans*-carveterpin, melting at 126°–127°, was discovered by Baeyer during his researches on i-sylvestrene (or "carvestrene").[10]

Sylveterpineol, the chief product of the action of dilute alkali on sylvestrene dihydrochloride, has been shown,[11] by study of its oxidation products to be a mixture of Δ^6-m-menthenol(8) and Δ^1-m-menthenol(8). The mixture distills at 214°. The menthenols obtained by synthesis, employing the Grignard reaction as described in the foregoing pages, are usually obtained quite pure. All of the six theoretically possible *meta*-menthenols, having the hydroxyl group in position (8) are known.[12] When these meta-menthenols are decom-

[8] Wallach, *Ann.* *357*, 73 (1907).
[9] Haworth, Perkin & Wallach, *J. Chem. Soc. 103*, 1234 (1913).
[10] *Ber. 27*, 3490 (1894).
[11] Haworth, Perkin & Wallach, *loc. cit.*
[12] Perkin, *J. Chem. Soc. 97*, 2129 (1910).

posed a mixture of hydrocarbons results except in the case of Δ^2 or Δ^3-m-menthenol(8), which can decompose with loss of water only in one way.



Δ^3-*m-menthenol(8)* $\Delta^{3.8(9)}$-*m-menthadiene*

This hydrocarbon is of interest as showing the effect of the conjugation of the two double bonds upon the physical properties, as compared with the isomeric *meta*-menthadienes.[13] Its physical properties closely resemble the similarly constituted $\Delta^{3.8(9)}$-p-menthadiene.

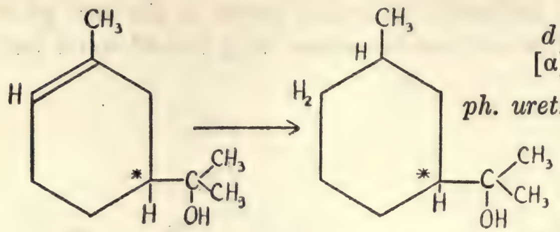
I. $\Delta^{2.8(9)}$—m-menthadiene [14]
II. $\Delta^{3:8(9)}$—m-menthadiene
III. $\Delta^{3.8(9)}$—p-menthadiene
IV. $\Delta^{1.8(9)}$—p-menthadiene (limonene).

	I.	*II.*	*III.*	*IV.*
Boiling-point	182°	181°–182°	184°–185°	175°–176°
$d\frac{20°}{20°}$	0.8624	0.8609	0.8580	0.8460
nD	1.5030	1.4975	1.4924	1.4746
M	46.6	46.3	46.02	45.23

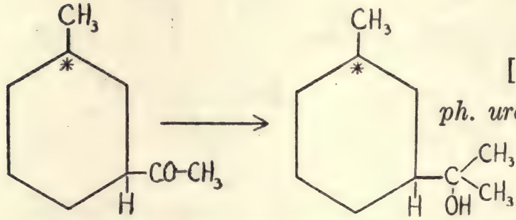
M. calc. for $C_{10}H_{16}/\!\!=^2$ 45.24.

Dihydrosylveterpineol [m-menthanol(8)] possesses two asymmetric carbon atoms and accordingly exists in two slightly different isomeric forms, the activity of one being due to the carbon atom (1), and in the isomer carbon atom (3) is active. The latter substance is obtained by the catalytic hydrogenation of sylveterpineol and the former is prepared by synthesis from 1-methyl-3-acetylcyclohexane.[15]

[13] Luff & Perkin, *J. Chem. Soc.* **97**, 2154 (1910).
[14] Haworth, Perkin & Wallach, *J. Chem. Soc.* **99**, 120 (1911).
[15] Haworth, Perkin & Wallach, *J. Chem. Soc.* **103**, 1228 (1913). Wallach, *Ann.* **381**, 51 (1911).

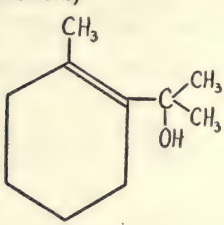


$d(3)$ form,
$[\alpha]_D + 10.35$
ph. urethane, M.-P. 77°

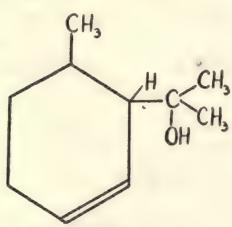


$d(1)$ form,
$[\alpha]_D + 1.96°$
ph. urethane, M.-P. 83°

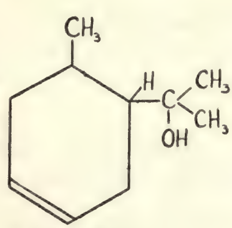
Ortho-Menthane Derivatives: Menthenols and menthadienes of the *ortho* series have not been found in nature but we have a fairly complete knowledge of them due largely to the systematic researches of Perkin, Jr., and his assistants. The methods of synthesis employed by Perkin to obtain the substances of this series are quite closely analogous to those already described in connection with the *para* and *meta*-menthane derivatives. Of the six possible *ortho*-menthenols, in which the hydroxyl group occupies postion (8), five are known. Their boiling-points under 30mm. pressure are given for the known *ortho*-menthenols,



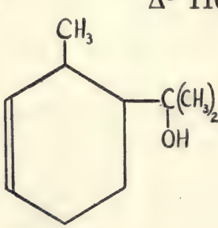
Δ^1 112°



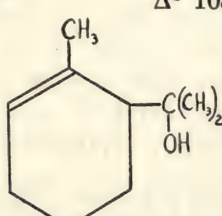
Δ^3 110°



Δ^4 108°

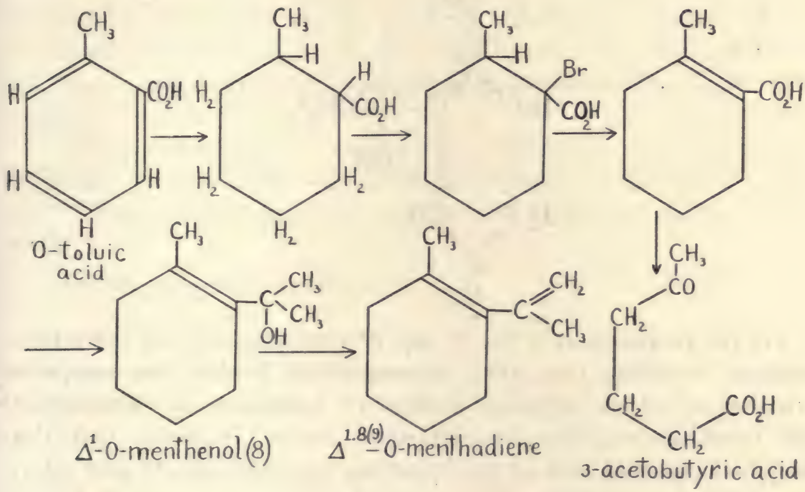


Δ^5 110°

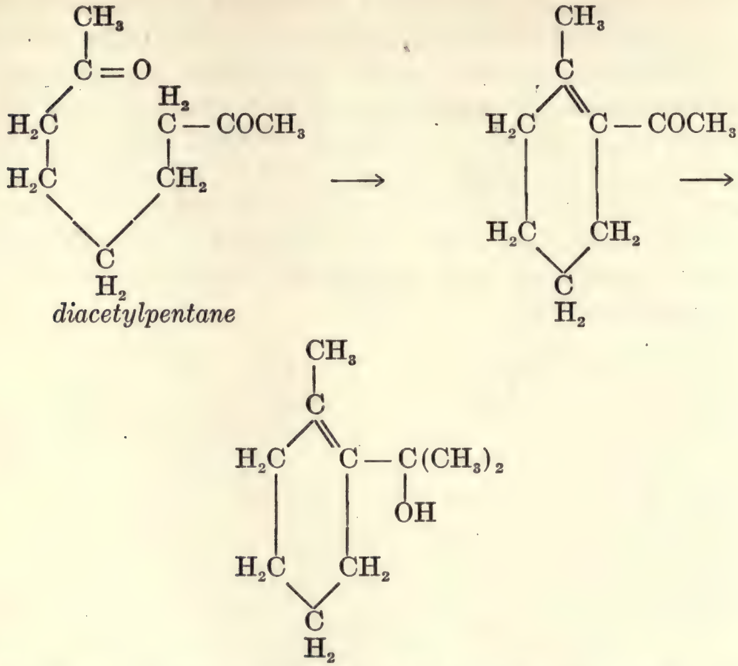


Δ^6 110°

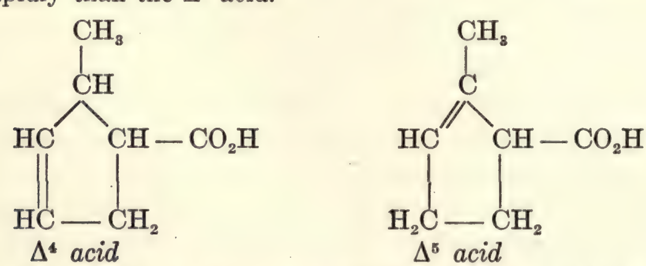
Like the m-menthenols, these of the ortho series have odors closely resembling a mixture of terpineol and menthol. No attempt has been made to resolve the synthetic inactive o-menthenols into their active *d* and *l* constituents. Δ^1-o-menthenol (8) was synthesized from ortho toluic acid, which will serve to illustrate a typical synthesis of this series. Reduction by sodium and amyl alcohol gave 1-methyl-cyclohexane-2-carboxylic acid which was then brominated and then decomposed to the unsaturated acid which was proven to be 1-methyl-Δ^1-cyclohexene-2-carboxylic acid by oxidation with permanganate to 3-acetobutyric acid.



As in the case of Δ^2-m-menthenol (8), this o-menthenol can decompose with the formation of a double bond in only one direction and accordingly the resulting $\Delta^{1.8(9)}$-o-menthadiene is quite pure. It exhibits the usual characteristics of a hydrocarbon containing conjugated double bonds, combines with only one molecule of a halogen or halogen acid, exhibits exaltation of the molecular refraction, has a boiling-point higher than its isomers which do not have their double bonds in conjugated position, resinifies rapidly in contact with air or on warming with metallic sodium, etc. The same o-menthenol and o-menthadiene was synthesized in quite a different manner by condensing diacetylpentane (by means of sulfuric acid) and treating the resulting unsaturated ketone with magnesium-methyl-iodide in the usual manner.

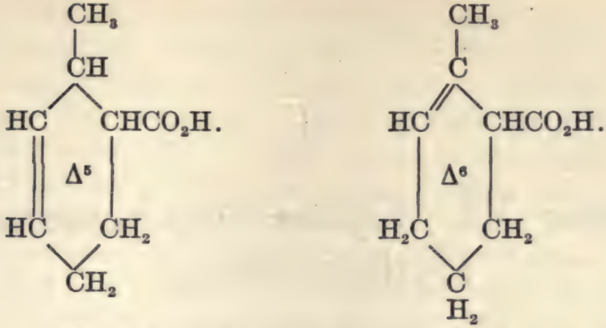


For the preparation of the Δ^5 and Δ^6-o-menthenols and the o-menthadienes resulting from their decomposition Perkin was compelled to make use of an ingenious method of separating the 1-methyl-Δ^5 and 1-methyl-Δ^6-cyclohexenecarboxylic acids. Haworth and Perkin [16] had observed that of the following two acids the Δ^4 acid esterifies much more rapidly and the ester is hydrolyzed or saponified much more rapidly than the Δ^5 acid.



It was found that the methylcyclohexenecarboxylic acids showed a parallel behavior, the 6-acid esterifying much less rapidly than the 5-acid.

[16] *J. Chem. Soc.* 93, 577 (1908).



Δ^5-esterifies much more rapidly than Δ^6. Perkin was able to effect a fractional separation of these two acids by making use of this fact, and then synthesized the corresponding o-menthenols in the usual manner.

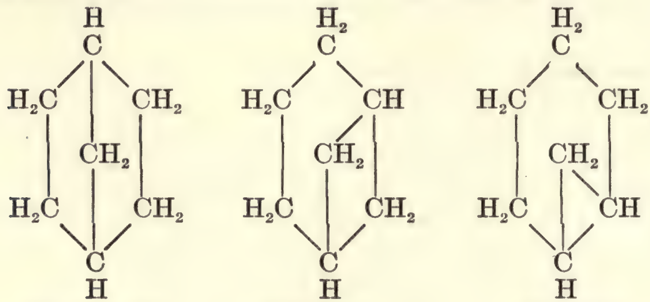
O-Menthane-5-One: The first o-menthanone to be described was prepared by reduction of 1-methyl-2-isopropyl-Δ^6-cyclohexene-5-one.[17] This o-menthone boils at 204° and yields an oxime melting at 75°.

[17] Kötz and Anger, *Ber.* 44, 466 (1911).

Chapter XI. Cyclic Non-benzenoid Hydrocarbons.

Bicyclic and Tricyclic Non-benzenoid Hydrocarbons.

Camphene, bornylene and the pinenes are bicyclic hydrocarbons which might be considered as derivatives of cyclohexane but on account of their importance and the volume of their literature these hydrocarbons are considered in separate chapters. The three simplest bridged cyclohexane hydrocarbons are not known.



norcamphane *norpinane* *norcarane*

These hypothetical hydrocarbons have the cyclic structures of camphene, pinene and carene respectively. A ketone having the structure of norpinane has recently been made by heating the calcium salt of cyclohexane-1.3-dicarboxylic acid and it would probably not prove difficult to prepare the hydrocarbon from the ketone. Norpinane and particularly norcarane would probably prove to be unstable, lacking the *gem.* dimethyl group.[1]

When indene is reduced by sodium and alcohol, two atoms of hydrogen are added, forming hydrindene, a large number of derivatives of which are known. Willstätter and King noted that the double

[1] Cf. Ingold, *J. Chem. Soc.* *119*, 952 (1921).

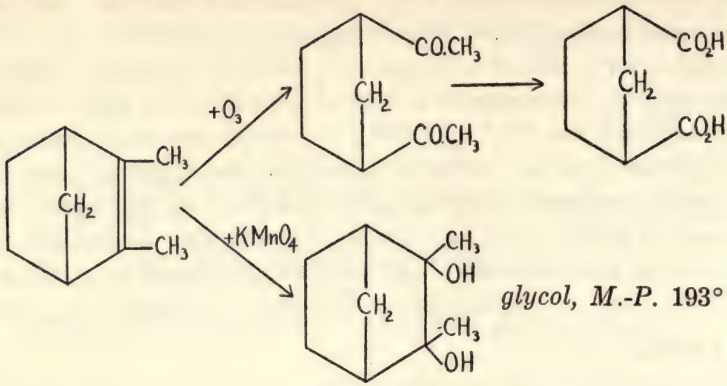
bond in styrene was reduced by hydrogen and platinum very much more rapidly than the benzene ring and by interrupting the hydrogenation good yields of ethylbenzene could be obtained. Similarly, indene may be hydrogenated in contact with nickel at 200° to hydrindene,[2] boiling-point 177°. At 300°, in contact with nickel and hydrogen, hydrindene is not further hydrogenated but is partly decomposed and partly converted to indene and hydrogen. At 250°–260°, in the presence of nickel oxide and hydrogen under 110 atmospheres pressure, indene and hydrindene are completely reduced to octohydroindene,[3] a stable oil, boiling-point 165°–167° (757mm.), $d_{20°}$ 0.8334, n_D 1.46287.

Santene, C_9H_{14}. This hydrocarbon, discovered in oil of sandalwood by Müller[4] and in Siberian pine-needle oil by Aschan[5] is noteworthy as being one of the few hydrocarbons, occurring in essential oils, having other than ten or fifteen carbon atoms. Santene is characterized by the formation of a nitrosochloride melting at 109°–110°, a nitrosite melting at 125° and a hydrochloride melting at 80°–81°. The alcohol, santenol, formed by treating with glacial acetic and sulfuric acids (Bertram and Walbaum's method) melts at 97°–98° and distills at 195°–196° (phenylurethane melting at 61°–62°). The acetate has an odor resembling bornyl acetate and distills at 215°–219°. The physical properties of santene noted by different observers are as follows.

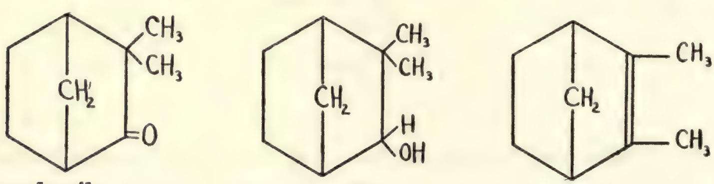
	I[6]	*II*[7]
Boiling-point	31.°–33.°(9mm.)	140.°
$d_{20°}$	0.863	0.8698(15°)
n_D	1.46658	1.4696

The constitution of santene has been shown by Semmler and Bartelt[8] by means of oxidation by ozone and by permanganate in dilute acetone to be as represented in the following,

[2] Padoa & Fabris, *J. Chem. Soc. Abs. 1908,* I, 255.
[3] Ipatiev, *J. Russ. Phys.-Chem. Soc. 45,* 994 (1913).
[4] *Arch. Pharm. 238,* 366 (1900).
[5] *Ber. 40,* 4918 (1907).
[6] Santene from sandal-wood oil, Semmler, *Ber. 40,* 4591 (1907).
[7] Santene from Siberian pine-needle oil, Ashcan, *Ber. 40,* 4918 (1907).
[8] *Ber. 41,* 385, 866 (1908).



the constitution being clearly indicated by the formation of cyclopentane *trans*-dicarboxylic acid melting-point 86°, which acid was previously known. The formation of santene from camphenilone has recently been accomplished by Komppa and Hintikka[9] by decomposing the corresponding alcohol, camphenilol, by sodium acid sulfate and also by heating camphenilyl chloride with aniline. A mixture of hydrocarbons is obtained but santene is the principal product. A little confusion is cleared up by Komppa and Hintikka by showing that santenol is identical with isocamphenilol and Semmler's π-norborneol, and that santenone is identical with isocamphenilone and Semmler's π-norcamphor. In the conversion of camphenilone or camphenilol a rearrangement occurs, such as is frequently observed among the terpenes and cyclohexane derivatives.



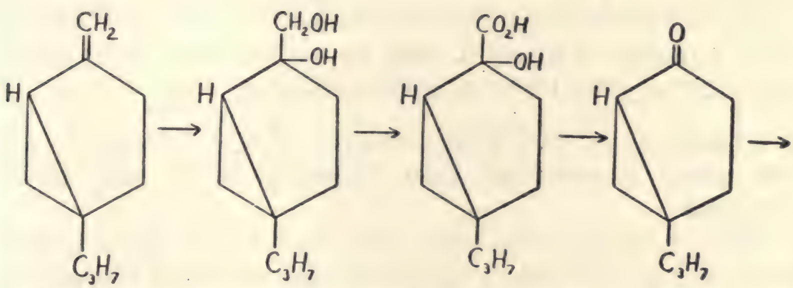
camphenilone *camphenilol* *santene*

Sabinene and Thujene may be considered as derivatives of paramenthane but they are both bicyclic and the bridged ring, common to both hydrocarbons, is a three carbon ring. Thujene (Semmler's tan-

[9] *Bull. soc. chim.* **21**, 13 (1917).

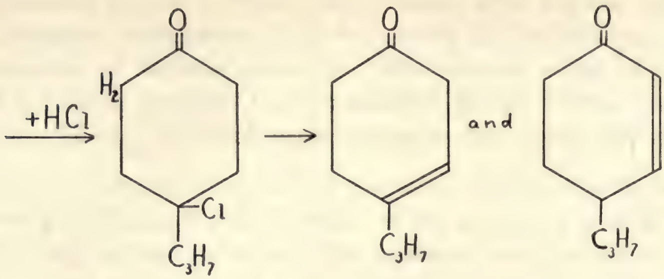
acetene) has not been found in any essential oil but sabinene occurs in the essential oil of savin and as a subordinate constituent in a number of other essential oils. Sabinene purified by fractional distillation, carried out by Schimmel and Company, showed a boiling-point of 163°–164° and an optical rotation of $[\alpha]_D + 63°$. Although the active hydrocarbon does not appear to have been obtained in a high degree of purity, it can be differentiated from other hydrocarbons of approximately this boiling-point, by its low specific gravity 0.8480 (15°). The molecular refraction owes its exaltation over the calculated value $C_{10}H_{16}/\!=^1$ to the presence of the three carbon ring. M (observed) 44.88, calculated, 43.53. It is readily converted to 1.4-terpin, terpinenol (4) and terpinene by the action of dilute sulfuric acid.

On oxidation by alkaline permanganate sabinene behaves very much like β-pinene and other substances having a semicyclic methene group; it yields first sabineneglycol (melting-point 54°), then sabinenic acid, the sparingly soluble nature of the sodium salt making its isolation easy.[10] Sabinenic acid melts at 57° and on further oxidation by lead peroxide and sulfuric acid yields sabina ketone.[11] The three carbon ring in sabina ketone is readily broken by hydrogen chloride in methyl alcohol and when the product is heated with aniline two isopropylcyclohexenones are produced. These ketones have been useful as serving for the synthesis of α-terpinene and α and β-phellandrene.



sabinene | *glycol M.-P. 54°* | *sabinenic acid M.-P. 57°* | *sabina ketone*

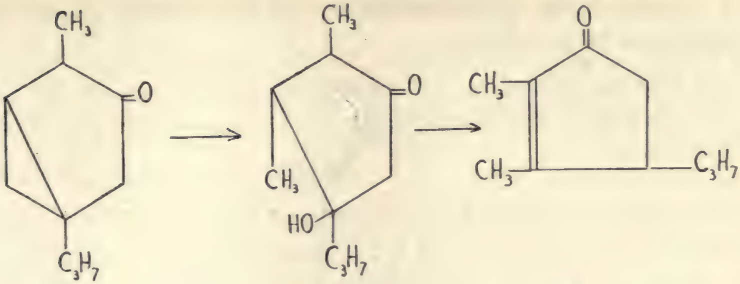
[10] Wallach, *Ann.* *359*, 266 (1908).
[11] Sabina ketone boils at 218°-219° and yields a semicarbazone melting at 141°-142°.



Thujene has been made indirectly from thujone, a ketone occuring in the oils of thuja, wormwood, tansy and sage. (The ketone has also been called tanacetone.) The ketone can be isolated by its bisulfite compound, using ammonium bisulfite and adding a little alcohol to increase the solubility of the ketone, and allowing to stand. The ketone may be liberated from the crystalline bisulfite compound by adding alkali and distilling with steam. There are two physically isomeric thujones, designated as α and β, and when they occur together they can be separated by fractional crystallization of the semicarbazones and regeneration of the ketones from the purified semicarbazones. The α-thujone, which is the chief ketone in thuja oil, boils at 200°–201°, specific gravity 0.9125, $[\alpha]_D - 10° 23'$ and n_D 1.4510. It appears to yield two dextro-rotatory semicarbazones melting at 110° and 186°–188°. Heating with alcoholic caustic alkali or alcoholic sulfuric acid converts α-thujone partially into β-thujone. When β-thujone is liberated from its semicarbazone (melting-point 170°–172° or 174°–176°) it is dextro-rotatory $[\alpha]_D + 76.16°$. Its oxime melts at 54°–55°. The conversion of α to β-thujone by alcoholic alkali is reversible. Both ketones yield the same bisulfite compound.

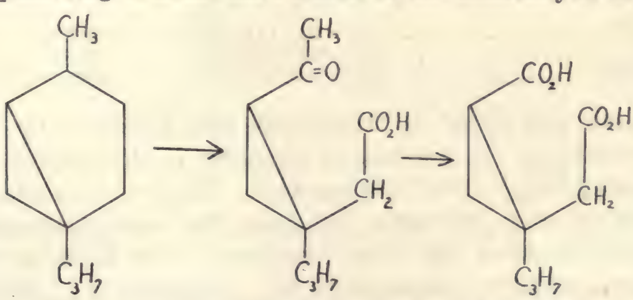
When the three-carbon ring of thujone is broken by heating with 40 per cent sulfuric acid an isomeric ketone, isothujone (boiling-point 231°–232°, d 0.9285) is formed, which change is represented by Wallach [12] and by Semmler [13] as follows,

[12] *Ann.* *323*, 371 (1902).
[13] *Ber.* *33*, 275, 2454 (1900).



thujone *isothujone*

Hydrogen chloride breaks the three-carbon ring in a different manner, α-thujene giving terpinene dihydrochloride.[14] Isothujone yields two physically isomeric thujamenthols according to whether the reduction is carried out by sodium and alcohol (α-thujamenthol, boiling-point 212°–214°, d $_{19°}$ 0.8990) or by hydrogen and palladium which yields β-thujamenthone and then by farther reduction by alcohol and sodium β-thujamenthone[15] yields the β-alcohol, which boils about 2° higher than the α-form. Thujone may be reduced to the corresponding alcohol, thujyl alcohol (boiling-point 210°–212°, d $_{20°}$ 0.9265), which alcohol is also formed by the action of nitrous acid on thujyl amine (the yields of alcohol by this reaction in most cases are very poor). Thujylamine is obtained in the usual manner, by reduction of thujone oxime. Oxidation of thujone yields first a keto acid, melting-point 75°–76°, and then by further oxidation a dicarboxylic acid melting at 141°–142°, both still retaining the three carbon ring but the cyclopropane ring is much more stable in the dicarboxylic acid.

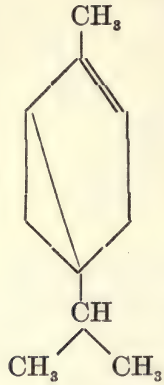


α-thujaketonic acid *M.-P.* 75°–76° *labil*

α-dicarboxylic acid *M.-P.* 141°–142° *stable*

[14] Wallach, *Ann.* *360*, 97.
[15] *Ibid.*

The constitution of thujene has not yet been clearly shown but it is believed to be as follows,



The physical properties of the hydrocarbon, prepared by different methods, indicate that "thujene" is probably a mixture of hydrocarbons, one of which probably has the constitution shown above. The name was formerly applied to the hydrocarbon made by the dry distillation of the hydrochloride of thujylamine or isothujylamine. Tschugaeff prepared thujene by heating thujyl xanthogenate, and also by heating and decomposing trimethylthujyl-ammonium hydroxide, the latter method giving a hydrocarbon of considerably higher optical rotation than the former. The highest rotation observed is that noted by Kondakow and Skworzow,[16] i.e., + 109°. The following physical properties have been noted,

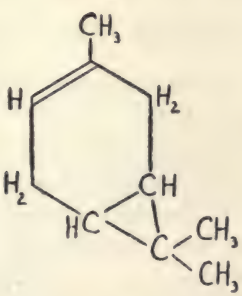
Observer	*Boiling-Point*	*Density 15°*	n_D
Semmler[17]	60°– 63° (14mm.)	0.8508	1.4760
Wallach	170°–172° (760mm.)	0.8360	1.47145
Tschugaeff[18]	151°–152° (670mm.)	0.8275	1.45042

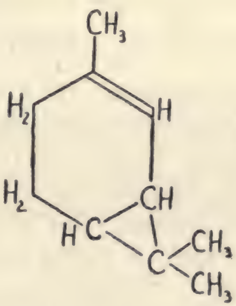
Thujane was made by Tschugaeff and Formin[19] by catalytic hydrogenation, in the presence of platinum, of the thujene made by decomposing thujylmethyl xanthogenate. Thujane is readily oxidized by permanganate. Sabinene also gives the same hydrocarbon by hydrogenation under the same conditions. The following physical properties were noted, boiling-point 157° (758 mm.), $d_{16°}$ 0.8190, Mol.

[16] *Chem. Zentr. 1910*, II, 467.
[17] *Ber. 25*, 3345 (1892).
[18] *Ber. 33*, 3118 (1900).
[19] *Compt. rend. 151*, 1058 (1910).

Refraction$_D$ 44.54 to 44.80, calculated 43.92, the difference being attributed to the presence of the cyclopropane ring. Thujane prepared by Kishner[20] from thujone by his hydrazine method showed the following physical properties, boiling-point 157.5° (741 mm.), $d_{20°}$ 0.8164, $[\alpha]_D + 53.41$, n_D 1.4398.

Carene: This terpene, recently found in Indian turpentine (from *Pinus longifolia*, Roxb.) is one of the few hydrocarbons occurring in nature which contains a three-carbon ring. It has frequently been noted that this turpentine contained a terpene which yields sylvestrene hydrochloride and it is usually stated that sylvestrene is present in this oil, although Robinson[21] stated that the terpene was probably an isomer of sylvestrene. Simonsen[22] isolated the hydrocarbon, boiling-point 168°–169° (750 mm.) by fractional distillation, and had no difficulty in preparing d-sylvestrene hydrochloride from this fraction. The liquid hydrochloride mixture gave sylvestrene and dipentene on heating with sodium acetate in acetic acid. Oxidation by permanganate gave a glycol melting at 69°–70° which apparently contains no primary alcohol group indicating the absence of the methene group. Oxidation by permanganate under the conditions recommended by Baeyer and Ipatiev gave trans-caronic acid, from which facts Simonsen concludes that carene has one of the two following structures, or is perhaps a mixture of the two.





d. Carene is slightly dextro-rotatory, $[\alpha]_D + 7.69°$, $D\frac{30°}{30°}$ 0.8586, $n\frac{30°}{D}$ 1.469 and from the refractive index M 44.23; M calculated for

[20] *J. Russ. Phys.-Chem. Soc.* 42, 1198 (1910).
[21] *Proc. Chem. Soc.* 27, 247 (1911).
[22] *J. Chem. Soc.* 117, 570 (1920).

$C_{10}H_{16}/=^1 = 43.5$ and adding the increment usually observed in cases where a cyclopropane ring is present M calc. becomes $43.5 + 0.69 = 44.19$.

Naphthalene is readily hydrogenated in the presence of finely divided platinum. When *dihydronaphthalene* is employed as the raw material, two atoms of hydrogen are very rapidly taken up and if the hydrogenation is then interrupted a good yield of tetrahydronaphthalene can be obtained but when starting with naphthalene and stopping the operation after four atoms of hydrogen had been taken up, the product was found to be a mixture of unchanged naphthalene and decahydronaphthalene.[23]

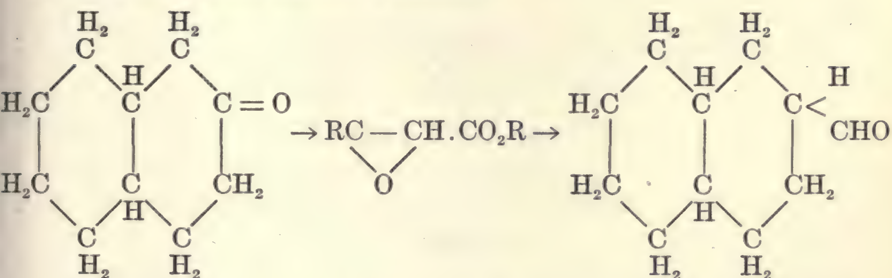
Tetrahydronaphthalene and the completely hydrogenated decahydronaphthalene were widely used in Europe, during the war period, as solvents, particularly as paint and varnish thinners.[24] A mixture of the hydrocarbons is manufactured under various trade names. Their solvent values are not accurately known but they are miscible with petroleum oils and are good solvents for coumarone resin, many natural resins, waxes, fats and oils. Their manufacture appears to be carried out in accordance with the well-known conditions of hydrogenation, employing temperatures within the range 120°–150°, and pressures within the range 3 to 100 atmospheres.[25] A preliminary purification from sulfur compounds by heating with metallic sodium, or with sodium amide is advised.[26] Tetrahydronaphthalene distills at 205°–207°, $d_{15°}$ 0.975, flash-point 78°. Decahydronaphthalene distills at 189°–191°, $d_{20°}$ 0.8827, flash-point 57.3°.[27] Auwers [28] notes the molecular refraction (D line) of tetrahydronaphthalene as 42.91 and that of decahydronaphthalene as 43.85.

The action of bromine on tetrahydronaphthalene is of interest as indicating the relative ease of bromine substitution in the two types of rings. No reaction takes place in the dark except in the presence of a catalyst such as iron or iodine when substitution in the benzene ring takes place. At higher temperatures, or in the light, the reduced ring is rapidly attacked but the only product isolated was α β-dibromotetrahydronaphthalene [29] (melting-point 70°).

[23] Willstätter & King, *Ber. 46,* 527 (1913).
[24] Frydlender, *Rev. prod. chim. 23,* 437 (1920).
[25] Brit. Pat. 147,474 (1920).
[26] Brit. Pat. 147,488 (1920); 147,580 (1920).
[27] Vollman, *Färber Ztg. 24,* 1689 (1919).
[28] *Ber. 46,* 2988 (1913).
[29] v. Braun & Kirschbaum, *Ber. 54,* 597 (1921).

The alcohols α and β-naphthanol were prepared by Ipatiev by his high pressure method.[30] β-Naphthanol $C_{10}H_{17}.OH$ distills at 242°–244° and melts at 99°–100°; α-naphthanol, $C_{10}H_{17}OH$, distills at 245°–250° and melts at 57°–59°, but Mascarelli[31] states that this alcohol can be separated into two stereo-isomers melting at 75° and 103°. Both alcohols resemble cyclohexanol and the aliphatic secondary alcohols in their chemical behavior. Naphthane-2.2-diol has been obtained in *cis* and *trans* forms; by the action of dilute caustic potash on 2.2-dibromonaphthane the *cis* form melting at 160° is obtained, while silver acetate on the dibromide yields the *trans* diol, melting at 141°.[32]

The ketone β-naphthanone has been very little studied but evidently undergoes the reactions of ether alicyclic ketones. Darzens and Leroux[33] condensed β-naphthanone with chloroacetic ester in the presence of sodium ethylate to the glycidic ester, the free acid from which loses carbon dioxide on distillation giving β-naphthanoic aldehyde (boiling-point 95°–96° at 3 mm.).



α, α-*Dicyclohexylethane,* ⬡—CH_2CH_2—⬡ This hydrocarbon was made by Sabatier and Murat[34] by the hydrogenation of diphenylethane in the presence of catalytic nickel and hydrogen at 220°. Its physical properties are as follows: Boiling-point 256°–257°, $d_{20°}\,0.9271$, $n\frac{40°}{D}\,1.511$.

The Nomenclature of spiro and other bridged ring hydrocarbons is in a very unsatisfactory state and none of the systems thus far proposed are very satisfactory except for certain types or classes of hydrocarbons. Probably the most flexible and least confusing is that

[30] *Ber. 40,* 1288 (1907).
[31] *Chem. Abs. 1912,* 83.
[32] Leroux, *Compt. rend. 148,* 1614 (1909).
[33] *Compt. rend. 154,* 1812 (1912).
[34] *Compt. rend. 154,* 1771 (1912).

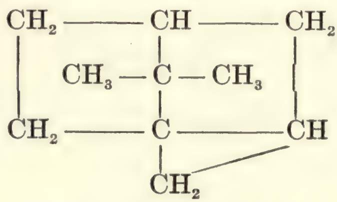
recently proposed by Beesley and Thorpe. The scheme advocated by Baeyer [35] rests upon the fact that all dicyclic systems contain three bridged rings which makes it possible to distinguish them by prefixed numerals such as (0.1.2), (1.2.3), (0.1.4) and so on, depending upon whether the "bridge" is formed by the linking of two tertiary carbon atoms (0), or whether it is itself formed by 1,2 or more carbon atoms. When Baeyer's system is extended to tricyclic substances it becomes exceedingly cumbersome and complex. The plans suggested by Borsche [36] and by Bredt and Savelsberg [37] are open to the objection that terms such as methylene are used to denote ring formation and not unsaturation, and that the names of the compounds do not necessarily indicate to which of the cyclic systems they belong. Thus pinene by these systems would be named as follows,

Borsche. 1-Methyl-1-Γ-$^{2(4)}$-dimethylmethylene-$\Delta^{1(6)}$-cyclohexene.

Bredt and Savelsberg: m-meso-methylene-4.4.2β-trimethylcyclo-$\Delta^{1.2\beta}$-hexene.

Beesley and Thorpe (see below): dimethylmethane-$\text{II}^{1.3}$-4-methyl-Δ^4-cyclohexene.

The hydrocarbon of the following structure,

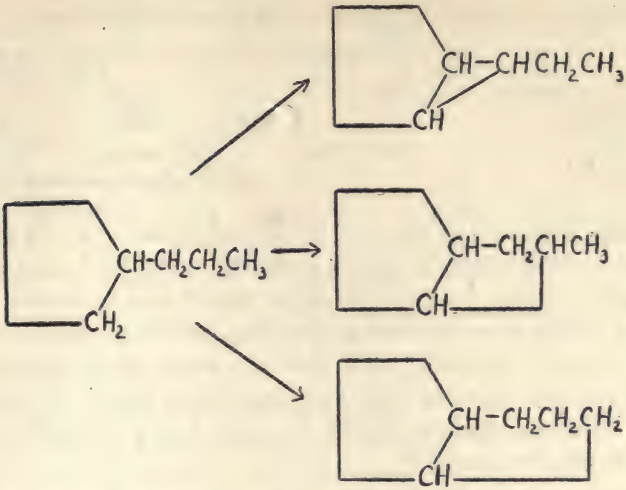


would be named, according to Bredt and Savelsberg, *p-meso*methylene-1.1-dimethylcyclohexane-amphi-$2^a.3^a$-methylene. By Beesley and Thorpe's system, the name would be methane-$\text{II}^{1.2}$-cyclohexane-$^{1.4}\text{II}$-dimethylmethane. Beesley and Thorpe's system appears to the writer to be much more easily grasped and easier to apply than the others,—and much more definite. It may be briefly outlined as follows:

A compound containing associated rings may be of two kinds.

A. It may be formed from a simple ring compound having a side chain of carbon atoms from which another ring is produced by a linking between another carbon atom of the ring and another of the side chain, thus:

[35] *Ber. 33,* 3771 (1900).
[36] *Ann. 377,* 70 (1910).
[37] *J. prakt. Chem.* (2) *97,* 1 (1918).



(1)

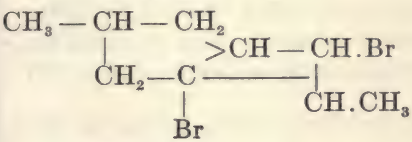
(2)

(3)

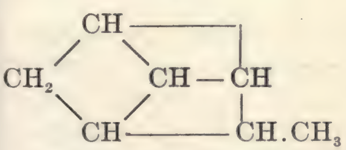
In these cases the side chain and the ring would be given their usual names, the number of linkings joining the two would be indicated by a Roman numeral, and the carbon atoms of the two series participating in the ring complex would be indicated by means of index figures on which the particular residue is placed. Thus, the above hydrocarbons (1), (2) and (3) would be named as follows,

(1) is Ethylmethane-$\mathrm{II}^{1.2}$— cyclopentane.
(2) is 2-Methylethane —$^{1.2}\mathrm{II}^{1.2}$— cyclopentane.
(3) is Propane —$^{1.3}\mathrm{II}^{1.2}$— cyclopentane.

The following is an example of the nomenclature of derivatives according to this system.

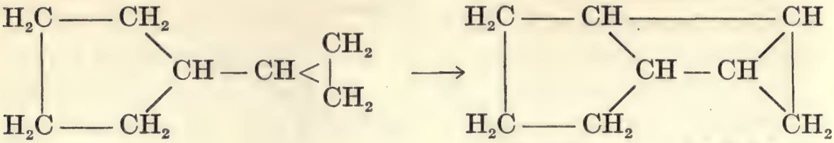


1-bromo-2-methylethane—
—$^{1.2}\ \mathrm{II}\ ^{1.2}$—2-bromo-4-methyl-cyclopentane.



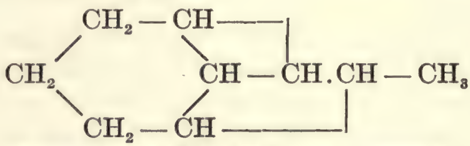
2-methylethane—$^{1.1.2}$—$\mathrm{III}^{1.2.4}$—
—cyclobutane.

B. The associated ring may be considered as formed by linking pairs of carbon atoms in a ring to which another ring is already attached, as for example, the following,



cyclopropane-$^{1.2}$ II $^{1.2}$-
-cyclopentane

The only rules which seem to be necessary are: (1) That one of the linked carbon atoms in the ring should be called 1, and that the corresponding carbon atom in the chain should also be called 1. The numbering would then proceed in the ring clockwise, and in the side chain in the usual manner. (2) That the name of the simplest portion of the chain entering into ring formation should be used first, and any attached groups should be named as derivatives of the simplest chain, for example,



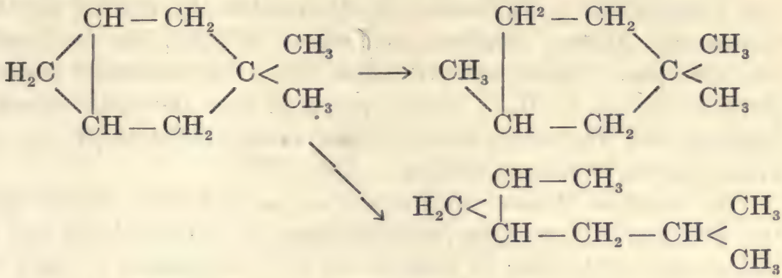
2-methyl—$^{1.2}$ III $^{1.2.6}$ —cyclohexane

For further details and possible extensions of the system to heterocyclic compounds, the original paper of Beesley and Thorpe should be consulted.[38]

3.3-Dimethyl-[0.1.3]-Dicyclohexane: This hydrocarbon was synthesized by Zelinski [39] by reducing 1.1-dimethylcyclohexane 3.5-dione to the corresponding diol, converting the diol to the corresponding dibromide by phosphorus tribromide and finally treating the dibromide with zinc dust in aqueous alcoholic solution. The chemical and physical properties of the resulting hydrocarbon, boiling-point 115° (corr), $d\frac{20°}{4°}$ 0.7962, $n\frac{20°}{D}$ 1.4331, particularly when compared with the isomeric 1.1-dimethyl-Δ^3-cyclohexene led Zelinsky to propose the bicyclic structure shown below. The three carbon ring is broken in two ways under different conditions. (1) By heating with hydriodic acid to give a hydrocarbon boiling at 115°–116° and indifferent to bromine and permanganate, probably 1.1.3-trimethylcyclopentane, and (2) by catalytic hydrogenation in the presence of platinum black,

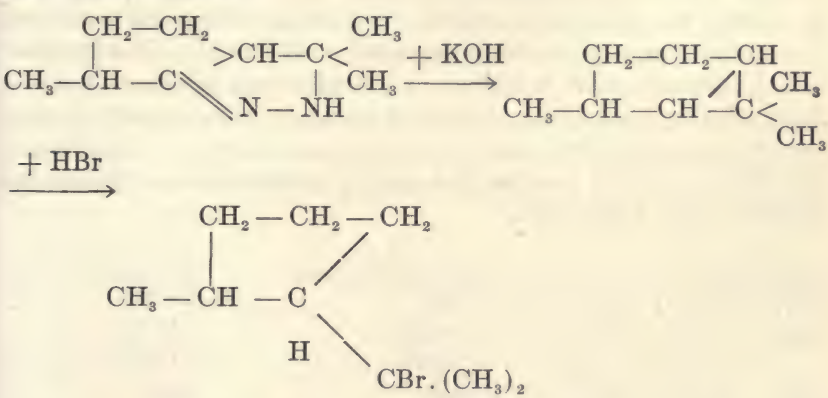
[38] *J. Chem. Soc.* *117,* 591 (1920).
[39] *Ber.* *46,* 1466 (1913).

yielding a hydrocarbon distilling at 109.5°–110.5°, which Zelinski claims is 1-methyl-2-isobutylcyclopropane.



The stability of this hydrocarbon to heat was not investigated but it is acted upon rather energetically by concentrated sulfuric acid.

A similar dicyclohexane derivative was discovered by Kishner,[40] in quite a different manner. When camphophorone is treated with hydrazine a pyrazolone base is first formed, which on heating with caustic potash yields the hydrocarbon *2.6.6.-trimethyl-*[0.1.3.]*-dicyclohexane.* It has a petroleum-like odor, boils at 140° (752 mm.), $d\frac{20°}{0°}$ 0.8223; does not decolorize permanganate, dissolves in fuming nitric acid and reacts with hydrogen bromide to give a bromomethylisopropylcyclopentane.



Caryophellene: The hydrocarbon oil described in the older literature under this name has been shown by Deussen and his students to be a mixture of at least two and probably three hydrocarbons. The

[40] *J. Russ. Phys.-Chem. Soc.* *44*, 849 (1912).

hydrocarbon mixture, isolated from copaiba balsam, clove oil and other essential oils, which distills at about 258°–261°, *d* 0.905 to 0.910 and which yields a crystalline dihydrochloride (by passing dry HCl into a dry ethereal solution) melting at 69°–70°, has been called caryophellene. The easiest crystalline derivative to prepare is caryophellene alcohol, $C_{15}H_{26}O$, readily prepared from the hydrocarbon by Bertram and Walbaum's method. The alcohol melts at 94°–96° and yields a phenylurethane, melting at 136°–137°.

The work of Deussen and others on caryophellene clearly shows the difficulties of working with mixtures of hydrocarbons and the almost impossible task of determining the constitution of such substances when present together and when they cannot easily be separated. It is worth while to examine Deussen's work as indicating to a limited extent the difficulties with which one would be confronted in attempting to ascertain the structure of the hydrocarbons occurring in the higher boiling distillates of petroleums.[41]

Wallach obtained a crystalline nitrosochloride melting at 161°–163° from the hydrocarbon fraction boiling at 250°–270°, derived from oil of cloves. Kremers and Schreiner prepared the nitrosochloride and after reacting with benzylamine, were able to separate the nitrolbenzylamine by fractional crystallization into fractions melting at 167° (named α-caryophellenenitrolbenzylamine) and at 128° (named β-caryophellenenitrolbenzylamine). Deussen[42] found that by heating the crude nitrosochloride in alcohol, cooling and separating the crystals, the melting-point was raised to 177°–179°. The behavior of the nitrosochlorides led Deussen to suspect the presence of one or more other hydrocarbons. Repeated fractional distillation[43] resolved the crude caryophellene into three fractions, fractions I and III having different optical rotation and slightly different boiling-points, but otherwise very much alike,

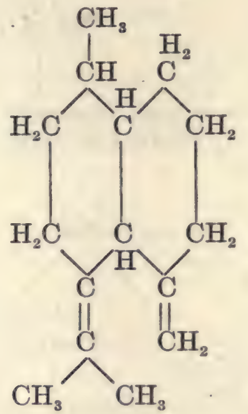
	I		*III*
Boiling-point	132.°–134.° (16mm.)		123.°–124.° (14.5mm.)
$[\alpha]_D$	—4.67°		—25.03°
d_{20}	0.90346		0.8990
n_D	0.49973		1.49617
MR	66.45		66.31
MR (for /=²)	....	66.15	....

[41] It is the writer's belief that the only practical way of throwing any light on the character of such petroleum hydrocarbons is to synthesize hydrocarbons of different types and compare the properties of such synthetic hydrocarbons with close cut petroleum fractions.

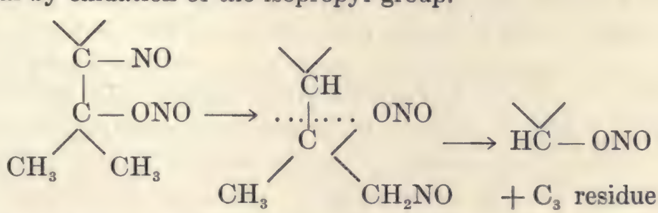
[42] *Ann.* *356,* 5 (1907).

[43] *Ann.* *359,* 246 (1908).

Fraction I. was believed to be inactive, so-called α-caryophellene contaminated with a small proportion of the lævo-β-caryophellene. The latter hydrocarbon yields a blue nitrosite from which Deussen concludes[44] (from Baeyer's work on terpinolene) that β-caryophellene contains a double bond of the type shown in the following structure, which he proposed.



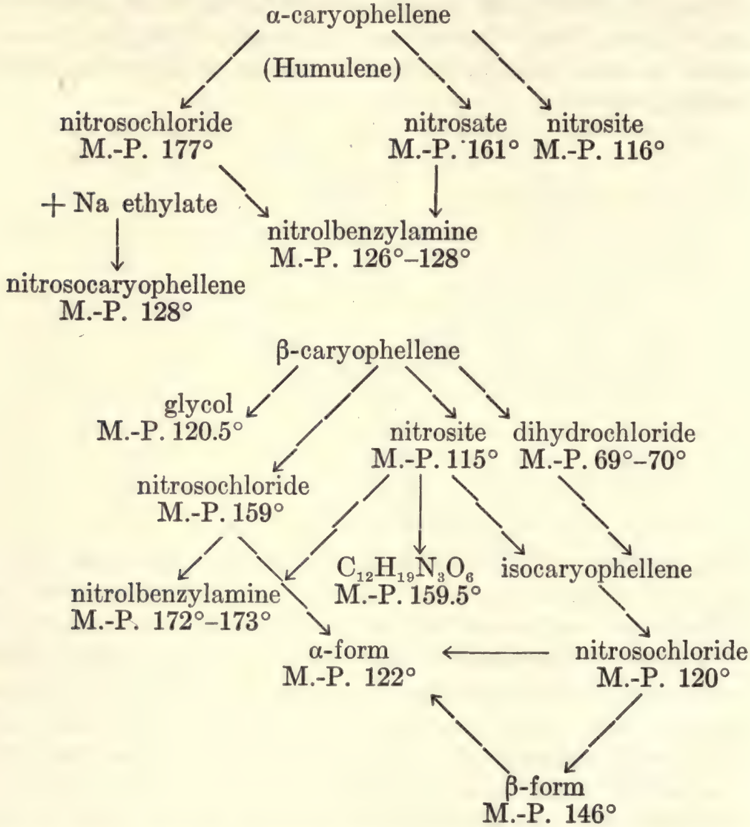
When an excess of N_2O_3 (from the reaction of arsenious acid and nitric acid) is passed into an ethereal solution of caryophellene a blue color first appears, followed by the formation of a voluminous yellowish white precipitate and the discharge of the blue color,[45] this behavior resembling the formation of caoutchouc nitrosite.[46] The voluminous precipitate from caryophellene crystallizes from ethyl acetate in silky needles melting with decomposition at 159°–160°, the separation of this substance being regarded by Deussen as a delicate test for β-caryophellene. The formation of this substance is attended by the removal by oxidation of the isopropyl group.



Deussen advanced this explanation of the change by reason of the fact that the product is soluble in alkali, a property only of primary

[44] *Ann.* *369*, 55 (1909).
[45] Deussen, *Ann.* *388*, 138 (1912).
[46] Harries, *Ann.* *383*, 198 (1911).

and secondary nitro derivatives. Deussen [47] represents the derivatives of α and β-caryophellene diagrammatically as follows,



Although Semmler and Mayer [48] have proposed structural formulæ for what he terms (using a curious nomenclature of his own) *Terp*-caryophellene and *Lim*-caryophellene, these structures can hardly be considered as proven and will not be given space in this brief review. The above outline will indicate the variety of the isomeric derivatives and the difficulty of clearing up the constitution of such mixtures of oils. *Humulene* is the name given by Chapman to a sesquiterpene fraction isolated from oil of hops, but Deussen considers it to be identical with α-caryophellene.

Cadinene is the name given to a hydrocarbon or rather a mixture of

[47] *Ann.* *369*, 41 (1910).
[48] *Ber.* *43*, 3451 (1910); *44*, 3651 (1911).

hydrocarbons occurring in camphor oil, cedar wood and other essential oils; it is characterized by the formation of a dihydrochloride melting at 117°–118° and this dihydrochloride may be prepared from the crude hydrocarbon mixture distilling at 260°–280°. Pure cadinene has never been obtained from natural oils but the sesquiterpene regenerated from the dihydrochloride (which is perhaps not identical with the natural hydrocarbon) is usually regarded as nearly pure "cadinene." The hydrocarbon may be prepared by decomposing the dihydrochloride by the usual methods, heating with alcoholic caustic alkali, with aniline, or with sodium acetate in acetic acid. The physical properties of regenerated cadinene are as follows,

	I[49]	II[50]	III[51]
Boiling-point	274.°–275.°	271.°–273.°	271.°–272.°
$d_{20°}$	0.918	0.9215(15°)	0.9183
$[\alpha]_D$	—98.56°	—105.° 30′	—111.°
n_D	1.50647		1.5073

Dextro-rotatory cadinene has been observed in the essential oil of the Atlas cedar.

Cadinene resinifies very rapidly and is very easily polymerized, an indication that the two double bonds are in conjugated positions. The dihydrobromide, melting-point 124°–125°, and the dihydroiodide, melting at 105°–106°, are best made in glacial acetic acid solution. By catalytic hydrogenation, in the presence of platinum, tetrahydrocadinene is produced, boiling at 125°–128° (10mm.), $d_{20°}$ 0.8838, n_D 1.48045.

The constitution of cadinene is not known.

By the distillation of galbanum resin Semmler and Jonas[52] obtained a sesquiterpene alcohol, cadinol, which on decomposition by potassium acid sulfate, formic acid or phthalic anhydride yields cadinene.

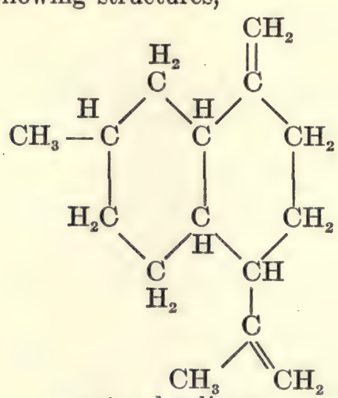
Selinene: A sesquiterpene distilling at 262°–269° was discovered in oil of celery seed by Ciamician and Silber[53] and the hydrocarbon was later recognized as a new hydrocarbon by Schimmel & Co.,[54] who characterized it by the formation of a dihydrochloride melting

[49] Wallach, *Ann.* *252,* 150 (1889); *271,* 297 (1892).
[50] Schimmel & Co.; Gildemeister, "Die Aetherischen Oele," Ed. II, Vol. I, 347.
[51] *J. Russ. Phys.-Chem. Soc.* *40,* 698 (1908).
[52] *Ber.* *47,* 2068 (1914). Cadinol distills at 155°-165° (15mm.), $d_{20°}$ 0.9720 $[\alpha]_D$ + 22°.
[53] *Ber.* *30,* 496 (1897).
[54] Schimmel & Co. Semi-Ann. Rep. *1910* (1), 32.

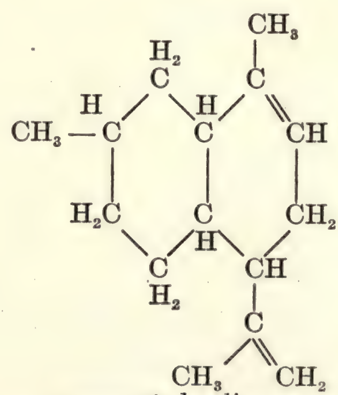
at 72°–74°. Semmler and Risse[55] prepared the dihydrochloride (by HCl into the ethereal solution) and regenerated what they regard as selinene, identical with the original hydrocarbon but purer, by decomposing the dihydrochloride by alcoholic caustic potash. The hydrocarbon thus obtained distills at 128°–132° (11 mm.), $d_{20°}$ 0.919, n_D 1.5092, $[\alpha]_D + 61°\ 36'$. Reduction by sodium and alcohol yields tetrahydroselinene having the following physical properties, boiling-point 125°–126° (10 mm.), $d_{20°}$ 0.888, $[\alpha]_D + 1°\ 12'$, n_D 1.48375.

By shaking the dihydrochloride with milk of lime for 36 hours at 95° an alcohol, selinol, $C_{15}H_{26}O$, is formed, which may be reduced by hydrogen (Willstätter's method) to dihydroselinol, $C_{15}H_{28}O$, melting-point 86°–87°.

On account of differences observed in the products obtained by treating natural and regenerated selinene with ozone and hydrolyzing the ozonides, Semmler regards natural selinene as a mixture of two hydrocarbons, both of which are believed to yield the same dihydrochloride. Semmler regards these two hydrocarbons as related to each other in the same way as α and β-pinene, the hydrocarbon predominating in natural selinene having a $>C=CH_2$ group, the double bond in the regenerated selinene being in the ring. Many will regard the constitutions proposed by Semmler as guesses, perhaps to be proven correct by further work but not clearly shown up to the present time. The two selinenes are bicyclic, contain two double bonds, and are believed by Semmler to be represented by the two following structures,



natural selinene



regenerated selinene

[55] Ber. 45, 3301 (1912); 46, 599 (1913).

Eudesmene: A sesquiterpene alcohol discovered by Smith [56] in numerous eucalyptus oils, and named eudesmol, yields the sesquiterpene eudesmene, $C_{15}H_{24}$, when decomposed by heating with 90 per cent formic acid. The alcohol is a bicyclic unsaturated alcohol, melting-point [57] 84° and distilling at 156° (10 mm.). It adds two atoms of hydrogen when reduced by Willstätter's method (hydrogen and platinum black in acetic acid solution) and the resulting dihydro-eudesmol melts at 82° and distills at 155°–160° (12.5mm.). When eudesmene or the alcohol is treated with hydrogen chloride in acetic acid a dihydrochloride, melting at 79°–80°, is formed. The dihydrobromide melts at 104°–105°. Eudesmene also combines with four atoms of hydrogen when reduced by the Willstätter method.[58] The physical properties of the two hydrocarbons are as follows,

	Eudesmene	*Tetrahydro-eudesmene*
Boiling-point	122.°–124.° (7mm.)	122.°–122.5° (7.5mm.)
$d_{20°}$	0.91964	0.8893
$[\alpha]_D$	+ 54.6°	+ 10.2°
$n_D^{20°}$	1.50874	0.48278

Santalenes: The sesquiterpene fraction of East Indian sandalwood oil apparently contains two hydrocarbons, which Guerbet [59] has called α and β-santalene. Their physical properties do not differ widely, α-santalene distilling about 10° lower than β-santalene. Both hydrocarbons give liquid hydrochlorides but α-santalene forms a nitrosochloride melting at 122° (nitrolpiperidide melting at 108°–109°) and β-santalene forms a mixture of two nitrosochlorides which can be separated by fractional crystallization to one melting at 106° and another melting at 152°. Probably neither hydrocarbon has ever been isolated in a very pure state. Semmler [60] gives the following physical properties of the two hydrocarbons.

	Boiling-Point	$d_{20°}$	$[\alpha]_D$	n_D
α-santalene	253°–254° (Corr.) .... 118°–120° (9mm.)	0.8984	–15°	1.491
β-santalene	263°–264° (Corr.) 125°–127° (9mm.)	0.892	–35°	1.4932

[56] *J. & Proc. Roy. Soc. N. S. W.* 33, 86 (1899).
[57] Semmler & Tobias, *Ber.* 46, 2026 (1913). The melting-point previously recorded by Semmler, *Ber.* 45, 1390 (1912), was 78°.
[58] Semmler & Risse, *Ber.* 46, 2303 (1913).
[59] *Bull. Soc. chim.* (3) 23, 217 (1900).
[60] *Ber.* 40, 3321 (1907).

Semmler[61] regards α-santalene as bicyclic and β-santalene as tricyclic.

Associated with the santalenes in sandal-wood oil are two alcohols, α and β-santalol, but their relation to the hydrocarbons has not been shown and Guerbet prefers to distinguish the hydrocarbons formed by the decomposition of the alcohols by the names α-*iso* and β-*iso*santalene. The santalols are both primary alcohols, yield an aldehyde, by oxidizing with chromic acid, whose semicarbazone melts at 230°. Oxidation with permanganate yields chiefly tricycloeksantalic acid, $C_{11}H_{16}O_2$, melting at 71°–72°. According to Guerbet α-santalol distills at 300°–301° and β-santalol at 309°–310°. The former is nearly inactive, $[\alpha]_D - 1.2°$ and β-santalol has the rotation $[\alpha]_D - 56°$. When α-santalol is reduced by hydrogen in the presence of platinum the hydroxyl group is replaced by hydrogen; the product is tetrahydrosantalene,[62] a bicyclic hydrocarbon, $C_{15}H_{28}$, distilling at 115°–116° (9 mm.). β-Santalol behaves similarly, giving mainly tetrahydrosantalene.

By heating *l.* α-phellandrene and isoprene together in a sealed tube, Semmler obtained a hydrocarbon $C_{15}H_{24}$ boiling-point 129°–132° (at 15 mm.), $d_{20°}$ 0.8976, n_D 1.4949, which he regarded as β-santalene. Limonene and isoprene under the same conditions do not react. In a series of such experiments Semmler showed that generally condensation of isoprene with the terpenes can be effected at about 275° but at 330° and higher, the sesquiterpenes are decomposed.[63]

Cedrene: This sesquiterpene, occurring in cedar-wood oil associated with the closely related alcohol, cedrenol, is of unknown constitution although considerable effort has been spent in research on this hydrocarbon. It forms a dihydrocedrene when catalytically reduced in the presence of platinum. Cedrene distills at 262°–263°, or 124° to 126° at 12 mm., $d_{20°}$ 0.9354, $[\alpha]_D$ $-55°$, n_D 1.50233. Oxidation by permanganate (in acetone solution) yields a glycol melting at 160°, also a diketone or ketoaldehyde of the empirical formula $C_{15}H_{24}O_2$ and a keto acid of unknown constitution, $C_{15}H_{24}O_3$ (oxime melting at 60°). By oxidation of cedrene by chromic acid in acetic acid solution a ketone, *cedrone*, is produced, this ketone having a strong odor of cedar wood, distills at 147°–150.5°, $d_{12.5°}$ 1.0110.[64]

[61] *Ber.* 1120 (1907).
[62] Semmler & Risse, *Ber.* *46*, 2303 (1913).
[63] *Ber.* *47*, 2252 (1914).
[64] Semmler & Hoffman, *Ber.* *46*, 768 (1913).

Cedar-wood oil appears to contain two sesquiterpene alcohols related to cedrene.[65]

Dihydrocedrene, obtained from natural cedrene by catalytic hydrogenation, distills at 122°–123° (10 mm.), d_{20° 0.9204, n_D 1.4929. No crystalline hydrochlorides or hydrobromides of cedrene are known.

Tricyclic non-benzenoid hydrocarbons have been made by the catalytic hydrogenation of tricyclic benzenoid hydrocarbons such as anthracene and phenanthrene. By the hydrogenation of phenanthrene at the remarkably high temperatures of 360°, under high pressure, Ipatiev[66] obtained the completely reduced hydrocarbon $C_{14}H_{24}$, which he calls perhydroanthracene. It is an oil distilling at 270°–276° and does not crystallize at 15°. It is inert to permanganate solution and bromine in the cold, and also practically unacted upon by sulfuric-nitric acid nitrating mixture.

Anthracene was reduced by Godchot[67] over nickel at 260° to tetrahydroanthracene, the constitution of which is unknown. It crystallizes from alcohol in plates melting at 89° and distilling at 309°. At a little higher temperature, 200°–205° octohydroanthracene, melting-point 71° and distilling at 292°–295°, is formed, and at 260°–270° and under about 125 atmospheres pressure Ipatiev[68] succeeded in reducing it to decahydroanthracene, melting-point 73°–74°, and finally to the completely reduced hydrocarbon, perhydroanthracene, an oily liquid.

Copæne: This name has been given by Semmler and Stenzel[69] to a sesquiterpene occurring, together with caryophellene, in African copaiba balsam. The hydrocarbon was separated by fractional distillation, its constants as thus isolated, being as follows, boiling-point 119°–120° (10mm.), d_{15° 0.9077, $[\alpha]_D$ —13.35°, n_D 1.48943. It gives a hydrochloride identical with that formed by cadinene. The new hydrocarbon is apparently tricyclic, combining with two atoms of hydrogen, by catalytic hydrogenation to give dihydrocopæne, $C_{15}H_{26}$ (boiling-point 118°–121° at 12 mm., n_D 1.47987, d_{18° 0.8926). Semmler has proposed a constitution for copæne.

Abietic Acid: Ordinary commercial rosin consists chiefly of abietic acid. Its constitution is not definitely known but it has been shown

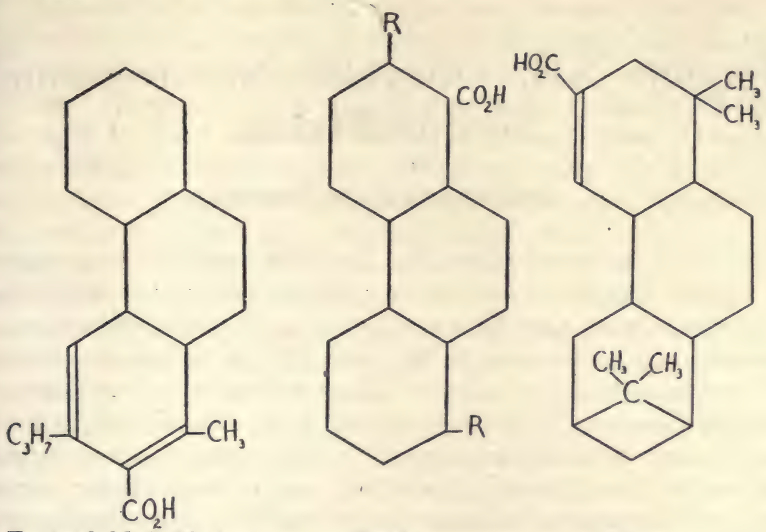
[65] Semmler & Mayer, *Ber.* *45*, 1384 (1912).
[66] *Ber.* *41*, 999 (1908).
[67] *Ann. chim. phys.* (8) *12*, 468 (1907).
[68] *Ber.* *41*, 996 (1908).
[69] *Ber.* *47*, 255 (1914).

to have the three ring carbon structure of phenanthrene. Heating with sulfur forms H_2S, carbon dioxide and *retene*, which hydrocarbon is believed to be a methyl isopropyl derivative of phenanthrene. The fossil substance fichtelite, $C_{18}H_{32}$, is regarded as completely reduced retene. Schulze [70] showed that rosin oil, obtained by the destructive distillation of rosin, contains hydrogenated retene derivatives and by oxidation 1.2.4-benzene tricarboxylic acid was obtained. The formation of this acid from abietic acid would show that the methyl and isopropyl groups are not attached to the same ring. Although combustion analyses of abietic acid, reported by different observers, agree almost equally well with the empirical formulæ $C_{19}H_{28}O_2$ and $C_{20}H_{30}O_2$, it may be pointed out that the formula $C_{19}H_{28}O_2$ agrees best with the known evidence that abietic acid has the carbon skeleton of phenanthrene together with a carboxyl group, a methyl and an isopropyl group, or 19 carbon atoms in all. Easterfield and Bagley [71] found that abietic acid was esterified with difficulty and therefore suggested that the methyl and isopropyl groups were in ortho positions with respect to the carboxyl group, thus assigning these two groups positions in one of the rings. Bucher [72] has reviewed the literature and, in view of the character of the oxidation products, states that one of the alkyl groups must be in position (8) and the other in position (2) or (3). Bucher also notes that an alkyl group in position (2) and the carboxyl group in position (1) would satisfy the condition which Easterfield and Bagley believed to be required by the slow rate of esterification. It need hardly be pointed out that much of this rests upon very slender evidence. As regards the difficulty of esterifying acids by saturating an alcoholic solution with hydrochloric acid gas, it may be pointed out that instances are known in which esterification with the aid of hydrogen chloride proceeds with difficulty, but with relative ease when the alcohol and acid are heated together. The formula $C_{19}H_{28}O_2$ and the tricyclic structure of reduced retene leaves two double bonds to be accounted for.

Grün,[73] who adheres to the $C_{20}H_{30}O_2$ formula, has recently proposed a constitution for abietic acid which has only one double bond [74]

[70] *Ann. 359,* 132 (1908).
[71] *J. Chem. Soc. 85,* 1238 (1904).
[72] *J. Am. Chem. Soc. 32,* 374 (1910).
[73] *J. Chem. Soc. Abs. 1921* (1), 344.
[74] Unpublished work of the writer has shown that when abietic acid, recrystallized from alcohol containing a little hydrochloric acid, is hydrogenated in dilute alcohol by Skita's method, the quantity of hydrogen absorbed is that required by *two* double bonds (within a very small experimental error). This, however, may nevertheless be in accord with Grün's formula and it may also be pointed out that Grün's formula may also account for the peculiar behavior noted in recrystallizing abietic acid. The

and has a bridged ring as in pinene, with which hydrocarbon abietic acid is associated in the natural oleo-resin. The formulæ which have been suggested are as follows,



Easterfield & Bagley *Bucher* *Grün*
(Double bonds not placed)

Rosin oil has been manufactured on a large scale and the heavier, neutral fractions used as a lubricant. As noted above such oils contain hydrogenated phenanthrene or retene derivatives. The crude oil contains about 30 per cent by volume of organic acids, has a marked greenish-blue fluorescence, and distills over a wide range of temperature. Its density varies from about 0.945 to 1.010. The lighter fractions, consisting of hydrocarbons of unknown character, are sometimes distilled and collected separately, being known industrially as rosin spirit. The fraction distilling at 343°–346° is believed to be a diterpene, $C_{20}H_{30}$. Rosin oil resinifies on air oxidation; its solubility in 96 per cent alcohol varies rather widely, i.e., 50 to 70 per cent at ordinary temperatures, depending upon the conditions under which the oil has been made.

bridged ring structure of Grün may account for this change by the rupture of the bridged ring by the hydrochloric acid.

Chapter XII. Bicyclic Non-benzenoid Hydrocarbons.

Turpentine and the Pinenes.

Probably the most outstanding fact with regard to turpentine is its rapidly decreasing production. This is having the result that turpentine is being replaced in many of its applications by light petroleum fractions, particularly in the case of paints and varnishes where it functions merely as a solvent. There are many industrial uses of turpentine, however, in which it appears to be indispensable, as in the manufacture of artificial camphor, terpineol and dammar varnish. The extent of the forests of the world, capable of producing turpentine, is well known and although the production of turpentine has been rapidly diminishing, reasonable sylviculture, as in France,[1] will insure a supply of turpentine easily adequate for chemical and other special purposes. The United States, the principal turpentine producing country, produced 27,073,000 gallons of oil of turpentine in 1914, but only 17,737,000 gallons in 1919 in spite of a considerable increase in the number of producing plants, much higher prices per gallon in 1919 and an increase in the output of "wood turpentine" and similar products of about one million gallons.[2] At the present time the United States produces 75 per cent of the world's turpentine supply. Not many years ago the greater part of the world's turpentine supply was derived from North Carolina alone, but the turpentine forests of that State have practically disappeared, North and South Carolina together now producing less than one per cent of the American output. It is worth while to call attention to these facts, and a knowledge of the physical properties and chemical behavior of the pinenes should be brought to bear upon every important industrial use of turpentine with the object of conserving the supply for uses for which it is indis-

[1] The pine tree plantations in Southwestern France cover an area of about 2.5 million acres, of which about 2 million acres are privately owned.

[2] Special Report on Turpentine, U. S. Bureau of the Census, Washington, May, 1921; Veitch, *U. S. Bur. Chem. Bull.* 898 (1920).

pensable and also affording relief by the substitution of cheaper material, so far as possible, in the case of consumers now handicapped by the high price of this solvent.

In the United States the only important sources are the long leaf yellow pine, *Pinus palustris*, and *Pinus heterophylla*, both of which yield turpentine oils consisting of more than 90 per cent of the two pinenes. The terms gum turpentine, gum spirits or spirits of turpentine refer to the volatile oil, distilled unchanged, from the natural oleoresin collected from the trees. Wood turpentine [3] made by distilling the wood in closed retorts with steam, or recovered by extracting the wood with a low boiling solvent, can be refined so as to replace turpentine for practically all solvent purposes, but when old stump wood is distilled an entirely different product is obtained, known commercially as "long leaf pine oil" or "pine oil," the chief constituent of which is terpineol [4] but other minor constituents which have been identified in it include the pinenes, *l*.limonene and dipentene, α and γ-terpinene, borneol, fenchyl alcohol and traces of cineol and camphor. The greater part of such pine oil distills from 190°–220° and is useful for the manufacture of terpin hydrate and terpineol, for the flotation of copper sulfide ores and in certain solvent mixtures and cleansing compositions. Rosin spirit is a term employed for the mixture of hydrocarbons obtained by the destructive distillation of rosin. It contains very little of the pinenes, boils over a wide range of temperature and usually contains organic acids of unknown character; it usually gives the Liebermann-Storch color reaction with acetic anhydride and sulfuric acid. It will be obvious from their composition that neither pine oil nor rosin spirit can be substituted for turpentine in the manufacture of artificial camphor.

Other products resembling turpentine find their way into commercial channels. "Recovered turpentine," a name sometimes applied to the mixture of terpenes, chiefly i-limonene, is produced by decomposing the liquid hydrochlorides obtained as a by-product in the manufacture of bornyl chloride and artificial camphor. Approximately 90 per cent of this product boils within the range 170°–180°, depending upon the rectification and purification of the product. The presence of chlorides, as indicated by the Beilstein or other halogen tests, is indicative of such an origin. The oils given off during the

[3] Cf. Frankforter, *J. Am. Chem. Soc.* *28*, 1467 (1906); Hawley & Palmer, U. S. Forest Service *Bull. 109* (1912); French & Withrow, *J. Ind. & Eng. Chem.* *6*, 148 (1914).
[4] Teeple, *J. Am. Chem. Soc.* *30*, 412 (1908).

melting of varnish gums are sometimes recovered but, even after good purification, have never found favor as thinners with paint and varnish manufacturers. The softer grades of Manila copal[5] yield 10 to 12 per cent of its weight of oil, largely limonene and i-limonene, during the first part of the fusion, up to about 330°. Fresh Queensland Kauri gum, from *Agathis robusta*, yields about 11.6 per cent of nearly pure α-pinene.[6]

Parry[7] gives the following physical properties of turpentine as the result of the examination of a large number of commercial samples.

Specific gravity at 15°	0.862– 0.870
n_D	1.468– 1.473
Initial boiling-point	154.° –155.5°
Distillate below 160°	72.% – 74.5%
Distillate below 170°	95.% – 97.5%
Iodine value, Hübl	360. –375.
Iodine value, Wijs	335. –350.

The optical rotatory power is subject to considerable variation. Herty[8] found the oil from *P. palustris* to vary from — 7° 26′ to + 18° 18′ and that from *P. heterophylla*, — 29° 26′ to + 0° 15′.

The volatile oils of several species of pine found in the western States have been examined by A. W. Schorger,[9] who finds that the turpentine from *P. Ponderosa* (Laws) and *P. Scopulorum* (Eng.) consists largely of β-pinene (q.v.): that from *P. Sabiniana* is practically pure n.heptane and that from *P. contorta* consists largely of β-phellandrene. These oils are not likely to become of commercial importance.

Pinus sylvestris is the chief source of Swedish and Russian turpentine and contains sylvestrene in addition to dipentene and β-pinene[10] and possibly α-pinene and *l.*camphene. Russian turpentine is a very indefinite product containing considerable proportions of phenolic or acid substances and oil boiling above 180°.

French oil of turpentine, which constitutes nearly 20 per cent of the world's supply, is derived from *Pinus pinaster (Pinus maritima)* and is a true pinene turpentine consisting chiefly[11] of *l.*-α-pinene, $[\alpha]_D$ — 20° to — 38°. It is suitable for the manufacture of artificial

[5] Brooks, *Philippine J. Sci. 1910,* 203.
[6] Baker & Smith, "A Research on the Pines of Australia," Sydney, 1910, p. 376.
[7] Chemistry of Essential Oils, Ed. 3, Vol. I, 17.
[8] *J. Am. Chem. Soc. 30,* 863 (1908).
[9] *Bull. 119,* U. S. Dept. Agriculture.
[10] *Chem. Ztg. 32,* 8 (1908).
[11] Darmois (*Chem. Zentr. 1910* [1], 30) concludes, from studies on its optical rotation, that this turpentine consists of approximately 62% α-pinene and 38% β-pinene.

camphor or other uses to which a true pinene oil can be put. With this brief review of the character of commercial turpentines the chemistry of the pinenes and their more important derivatives will be noted. With the elucidation of the constitution of β-pinene and its synthesis by Wallach in 1908, the chemistry of the pinenes is practically complete.

α-Pinene is one of the most widely distributed of the terpenes, having been found in the essential oils of a large number of Coniferæ, the grass oils, Lauraceæ, Labiatæ, etc.

When it occurs together with other terpenes in oils used for the manufacture of flavoring extracts or perfumes, it is common practice to separate the terpenes by making use of their lesser solubility in dilute alcohol,[12] as compared with the esters, alcohols, aldehydes and the like which give such oils their aromatic value. The resulting terpene-free oils can be dissolved in much more dilute alcohol, thereby effecting considerable saving in the preparation of these solutions.

Inactive α-pinene is one of the few terpenes which have been isolated in quite a pure condition. Fairly pure α-pinene can be obtained by fractional distillation of turpentine[13] but a purer product can be obtained by preparing the nitrosochloride, purifying this by fractional crystallization and regenerating the α-pinene by decomposing the nitrosochloride by aniline[14] in alcoholic solution. Such a sample described by Schimmel & Co.[15] had the following physical properties: boiling-point 154.5°–155°, d_{15° 0.8634, $n\frac{20^\circ}{D}$ 1.4664, optically inactive. The highest observed optical rotations of α-pinene are $[\alpha]_D + 51.52^\circ$ in the case of pinene isolated by A. W. Schorger[16] from the oil of the Port Orford cedar (*Chamæcyparis lawsoniana*). This is probably the purest natural α-pinene thus far discovered. A very pure *d.* α-pinene $[\alpha]_D + 48.4^\circ$ has been noted in the case of a specimen isolated from Greek turpentine (from the Aleppo pine, *P. halepensis*),[17] and a lævo-pinene $[\alpha]_D - 48.63^\circ$ from one of the eucalyptus oils, *E. lævopinea.*[18]

[12] Böcker, *J. prakt. Chem.* (2) *89,* 199 (1914); Vezes & Mouline, *Bull. soc. chim.* (3) *31,* 1043 (1904). See section on physical properties (solubility).

[13] Henderson & Sutherland recommend fractional distillation with steam, followed by ordinary distillation, taking the fraction boiling at 155°-156° as α-pinene. (*J. Chem. Soc. 101,* 2289 [1912]).

[14] Wallach, *Ann. 258,* 343 (1890).

[15] Gildemeister, "Die Aetherischen Oele," Ed. 2, Vol. 1, 308.

[16] *J. Ind. & Eng. Chem. 6,* 631 (1914).

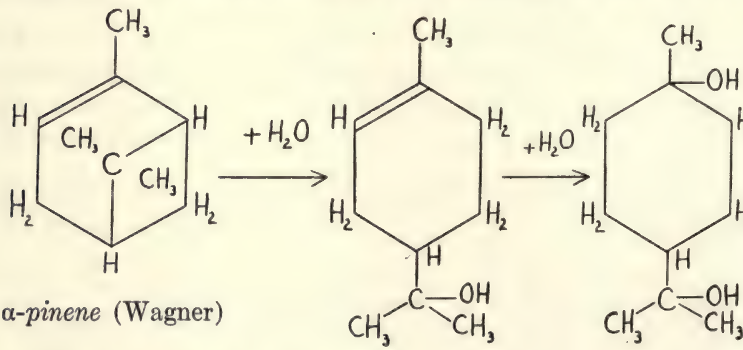
[17] Vèzes, *Bull. soc. chim.* (4) *5,* 932 (1909).

[18] Smith, *J. & Proc. Soc. N. S. W. 32,* 195 (1898).

Oils of high optical rotation give very poor yields of crystalline nitrosochloride.

α-Pinene is usually identified by preparing the nitrosochloride of the fraction boiling below 160°, which preparation is carried out by slowly adding concentrated hydrochloric acid to a strongly cooled solution of the hydrocarbon in glacial acetic acid and ethyl or amyl nitrite. On standing the crystalline nitrosochloride separates. After separating the crystals and recrystallization by dissolving in chloroform and precipitating with methyl alcohol, the nitrosochloride melts at 103° but the nitrolamines give melting-points which are more useful and reliable for identification purposes. The pinene nitrolpiperidine melts at 118°–119° and the nitrobenzylamine melts at 122°–123°. In preparing the nitrolpiperidine a small proportion of nitrosopinene is simultaneously formed.[19] In the case of pinene of high optical activity recourse may be had to oxidation by permanganate to the pinonic acids.[20] The hydrochloride (bornyl chloride) made by passing *dry* hydrogen chloride into cooled pinene, carefully dried by distillation over sodium, has also been employed for the detection of pinene although both α and β-pinenes give the same hydrochloride, melting-point 127°.

The constitution of α-pinene has been determined largely by a study of its oxidation products. One of the most important advances made in clearing up the chemistry of the terpenes was the recognition, first clearly set forth by Wagner, that the hydroxyl group in α-terpineol is in position (8) and not position (4). In this same remarkable communication of Wagner,[21] which was published in full in the Rus-

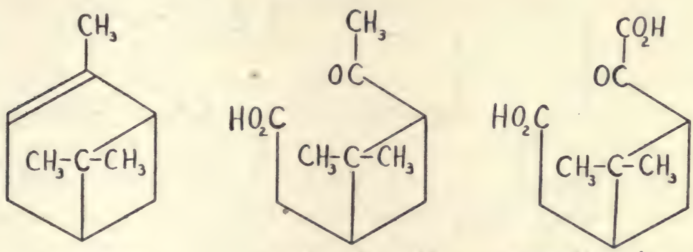


α-*pinene* (Wagner)

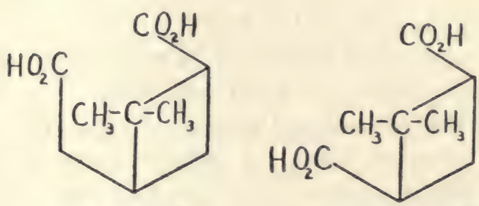
[19] Wallach, *Ann.* *245*, 252 (1888). Confirmed by Bushujew, *J. Russ. Phys.-Chem. Soc.* *41*, 1481 (1910).
[20] Schimmel & Co. Semi-Ann. Rep. *1909* (1), 120.
[21] *Ber.* *27*, 2270 (1894).

sian language, Wagner published what have proven to be the correct constitutions of limonene, carvone, dihydrocarvone, carone and α-pinene. According to Wagner's structure for α-pinene, the formation of α-terpineol and terpin is formulated as shown on the preceding page. Wagner seemed to have an almost uncanny ability to visualize the constitution of such substances.

Baeyer showed that a series of oxidation products obtained by him also are in accord with Wagner's α-pinene constitution, which oxidations he expressed as follows,[22]



α-pinene *α-pinonic acid* *pinoylformic acid*



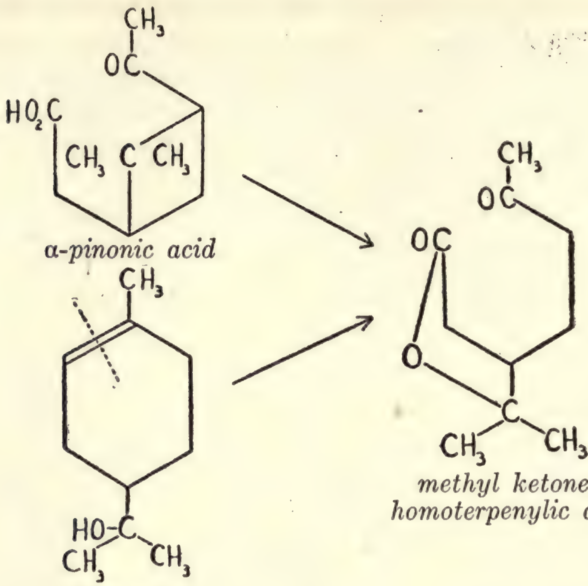
pinic acid *norpinic acid*[23]

Just as the four carbon ring in pinene is broken by dilute acids to form terpineol, so also is the four carbon ring in α-pinonic acid broken to give the methyl ketone of homoterpenylic acid, identical with the product of the oxidation of terpineol itself. (See page 426.)

α-Pinene is usually associated with the isomeric hydrocarbon, β-pinene, and oxidation by permanganate gives the products of oxida-

[22] *Ber.* *29*, 2775 (1896).

[23] The cyclobutane ring has about equal stability in pinene, pinonic acid and pinoylformic acid, being split with about equal ease by dilute acids. In pinic and norpinic acid it is very much more stable, this stablity being due apparently to the influence of the carboxyl group, parallel to the observations of Buchner on the effect of the carboxyl group on the stability of the cyclopropane ring.



α-pinonic acid

α-terpineol

methyl ketone of homoterpenylic acid [24]

tion characteristic of these two hydrocarbons. The oxidation is carried out [25] as follows: 5 cc. of the hydrocarbon are shaken for about three hours with an ice cold solution of 12 g. potassium permanganate, 2.5 g. caustic soda, 200 cc. of water and 500 g. ice. After 3 hours saturate with carbon dioxide and remove the volatile unoxidized oil by distillation with steam, filter and evaporate in a current of carbon dioxide to about 200 cc. and extract several times with chloroform. On further evaporation the first salt to separate out is sodium nopinate, which on acidifying gives crystalline nopinic acid, melting at 125°. This acid is characteristic for β-pinene. The sodium salt of pinonic acid is more soluble than the nopinate. Barbier and Grignard [26] have investigated the optically active forms of pinonic acid obtained by the oxidation of *d.* and *l.*α-pinene of high optical rotation. From *l.*pinene, $[\alpha]_D$ —37.2° *l.*pinonic acid was obtained, by permanganate oxidation and after distillation in vacuo, 189°–195° at 18 mm., separated in long crystals melting at 67°–69°, and $[\alpha]_D$ —90.5°. From

[24] The constitution of homoterpenylic and terpenylic acids is discussed in connection with terpineol and limonene.

[25] Schimmel & Co. Semi-Ann. Rep. *1910* (1), 165.

[26] *Compt. rend.* *147*, 597 (1908).

d.α-pinene, $[\alpha]_D + 39.4°$, they obtained a mixture of racemic and *d*.pinonic acids, the latter melting when recrystallized at 67°–68°, $[\alpha]_D + 89.0°$ and when mixed with the *l*.pinonic acid the racemic acid melting at 104° was obtained.

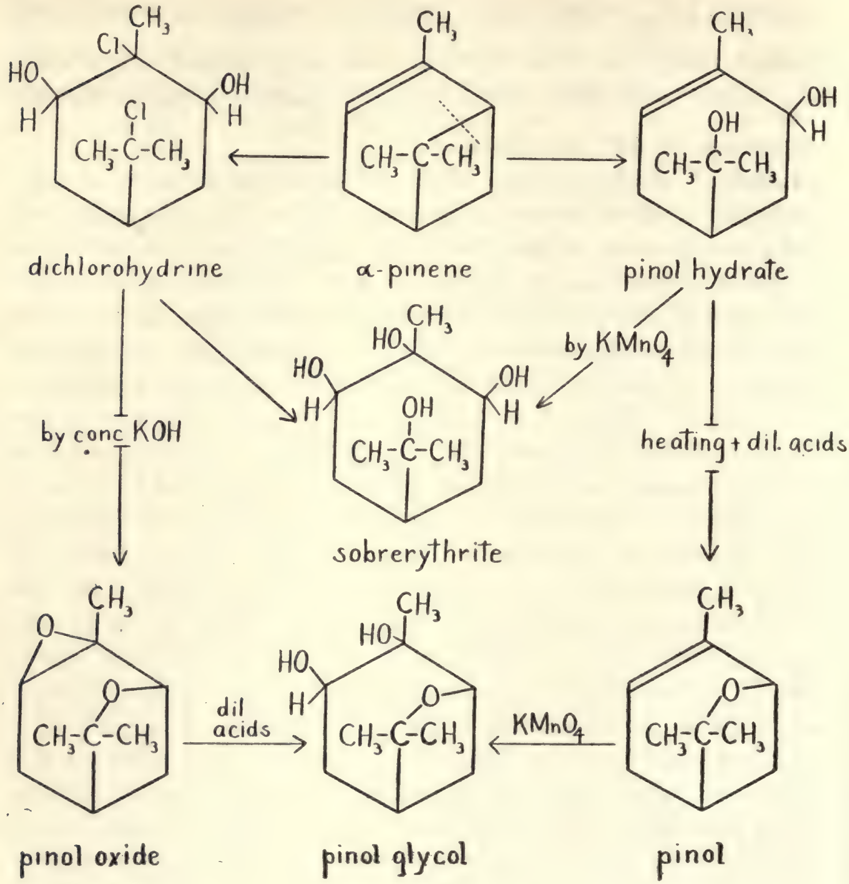
Harries[27] investigated the action of ozone on α-pinene and by heating the resulting ozonide with acetic acid to 90° obtained an oil boiling over the wide range of 100°–142° under 12 mm., from which he prepared a semicarbazone melting at 214°–215° which was "probably" pinonic aldehyde. On standing in contact with moist air, as in loosely stoppered containers, particularly in sunlight, turpentine or α-pinene is oxidized to pinol hydrate (sobrerol) which crystallizes from the oil.[28] From *d*. or *l*.turpentine the correspondingly active pinol hydrates, melting-point 150°, are obtained. The *d-l* hydrate is formed on treating pinol with hydrogen bromide followed by hydrolysis by alkali. The relations of pinol hydrate and pinol are indicated by the results on oxidizing with permanganate. Each adds two hydroxyl groups, pinol to form pinol glycol, $C_{10}H_{16}O.(OH)_2$ and the hydrate to form sobrerythrite[29] $C_{10}H_{16}(OH)_4$. Pinol glycol is also formed by the action of dilute acids on the dioxide, pinol oxide, $C_{10}H_{16}O_2$. Sobrerythrite is also formed by the action of hypochlorous acid on pinene and hydrolysis of the dichlorohydrin. In accord with the general behavior of the higher alkylene oxides (q.v.) concentrated alkalies convert the dichlorohydrin to the dioxide, pinol oxide, and on treating pinol oxide with dilute acids the 1.2 oxide is hydrolyzed to pinol glycol, leaving the oxide ring of four carbon atoms unchanged. Parallel with the behavior described in connection with cineol and other oxides, heating pinol hydrate with dilute acids causes the *formation* of the oxide pinol. These facts show clearly the relation between the number of carbon atoms in the oxide ring and their relative stability. (See figure on page 428.)

The behavior of turpentine or pinene on air oxidation is, in general, typical of the behavior of the olefines, including unsaturated petroleum oils. With all such substances air oxidation is accom-

[27] *Ber.* 42, 879 (1909).

[28] Formic acid is one of the products of the oxidation of turpentine by air and metal containers are accordingly sometimes corroded by old turpentine. Formic acid produced in this way is probably a product of the oxidation of β-pinene, not α-pinene.

[29] The sobrerythrite made from pinol hydrate melts at 156°; a stereoisomeric sobrerythrite made by the action of hypochlorous acid on pinene melts at 194°.



panied by the formation of organic peroxides, water, carbon dioxide, simple organic acids, resinous substances and other oxidation products among which alcohols, aldehydes and ketones have frequently been noted. The oxidizing power of old turpentine was observed by Schönbein and frequently investigated subsequently by others. The organic peroxides formed in this way are rapidly destroyed by heating to 140° and are hydrolyzed by water. As pointed out by Engler and Weissberg[81] the peroxides decompose, causing further oxidation of other

[80] The positions of the chlorine atoms and hydroxyl groups may be reversed; in the above constitution their positions are arbitrarily assigned. The dichlorohydrine of pinene may be a mixture of isomers, just as the addition of HOCl to propylene gives a mixture of $CH_3CHCl.CH_2OH$ and $CH_3CHOH.CH_2Cl$.

[81] Vorgänge der Autoxidation, 1904.

material[32] or unchanged oil or may even decompose breaking up the pinene molecule; the formation of peroxides cannot be observed above 160° although very rapid oxidation by air occurs at this temperature. It is well known that old oxidized turpentine "dries" more rapidly than freshly distilled turpentine and it is also a fact very generally observed that air oxidation greatly promotes resinification. Krumbhaar[33] noted that a sample of oil containing 0.002 g. active oxygen per cubic centimeter of turpentine "dried" very much faster than one containing 0.00057 g. active oxygen.[34] Among the products of the oxidation of turpentine by moist air in iron vessels is *verbenone* and the corresponding alcohol *verbenol*. From Grecian turpentine *d*.verbenone was obtained and from French turpentine *l*.verbenone and *d*.verbenol.[35] By the oxidation of pinene by benzoyl peroxide, an oxide is produced boiling at 102°–103° (50 mm.) which yields pinol hydrate on hydrolysis.[36] On oxidizing with hydrogen peroxide[37] or mercuric acetate the four-carbon ring is broken; the chief product of the action of hydrogen peroxide on pinene (by 30 per cent hydrogen peroxide and glacial acetic acid) is α-terpineol. Small proportions of borneol, a little menthane-1.4.8-triol and resinous material are also formed. The expected pineneglycol was not found. Oxidation by mercuric acetate gave pinol hydrate.[38]

By hydrogenating α-pinene in the presence of reduced nickel Sabatier[39] obtained pinane, boiling-point 166°, and in the presence of catalytic copper an impure pinane, boiling at 163°–170°, results.[40] Skita,[41] using platinum black, evidently did not get pure pinane, but Vavon[42] reports a quantitative yield of pinane, boiling-point 166° (755 mm.), $[\alpha]_D$ $+22.7°$ from *d*.pinene or $-21.3°$ for *l*.pinane from l.pinene from French turpentine, $d\frac{15°}{15°}$ 0.861, and solidifying-point about $-45°$. Böeseken[43] used pinene and platinum black in study-

[32] Sieburg (*Biochem. Zt. 43,* 280 [1913]), investigating the reputed efficacy of oxidized turpentine as an antidote for yellow phosphorus poisoning found that a compound of pinene and "phosphorous or hypophosphorous acid" was formed, but Willstätter and Sonnenfeld, *Ber. 47,* 3172 (1914), isolated a yellow crystalline compound, $C_{10}H_{16}P_2O_4$, by treating a solution of pinene and yellow phosphorus with dry air.

[33] *Farben Ztg. 18,* 1280 (1913).

[34] Determined by Klasson's method, *Chem. Abs. 5,* 3345.

[35] Blumann & Zeitschel, *Ber. 46,* 1178 (1913).

[36] Prileschajew, *Ber. 42,* 4811 (1909).

[37] Henderson & Sutherland, *J. Chem. Soc. 101,* 2288 (1912).

[38] Henderson & Agnew, *J. Chem. Soc. 95,* 285 (1909).

[39] *Compt. rend. 132,* 1254 (1901).

[40] Ipatiev, *Ber. 43,* 3546 (1910).

[41] *Ber. 45,* 3585 (1912).

[42] *Compt. rend. 149,* 997 (1909).

[43] *Rec. trav. chim. 35,* 288 (1916).

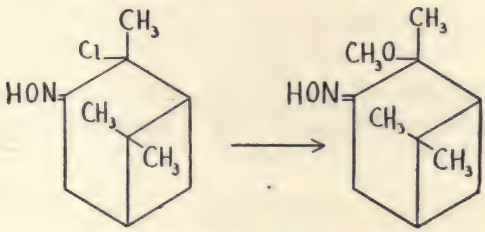
ing the effect of solvents on the rate of hydrogenation; in formic acid and in ethyl alcohol the hydrogenation is very slow and the catalyst becomes poisoned. Glacial acetic acid, as recommended by Willstätter, was most satisfactory. When using this solvent cyclopropane is slowly reduced to propane but under the same conditions the cyclobutane ring in pinene is not attacked. During the war Sabatier, Mailhe and Gaudion[44] investigated the decomposition of pinene at high temperatures in the presence of various metallic catalysts. Large scale experiments on several tons of turpentine, using catalytic copper at 550°, gave about 21 per cent of hydrocarbons capable of being nitrated. No dehydrogenation was observed at 350°. At 600° to 630° in the presence of copper the decomposition was extensive, forming considerable gas and a mixture of hydrocarbons boiling from 30° upwards and containing butylenes, amylenes, isoprene, hexylenes, aromatic hydrocarbons, etc., the mixture closely resembling the products resulting from the decomposition of petroleum oils under these conditions, or the light liquid condensed from Pintsch gas. Also as in the case of petroleum hydrocarbons, passing turpentine over nickel at 600° gave rapid deposition of carbon and much gas rich in hydrogen until the catalyst was rendered inoperative by the deposited carbon.

As noted above, in connection with the identification of α-pinene, pinenes of very high optical activity give no crystalline nitrosochloride when the usual method of preparation is followed, and Kremers[45] showed that the yield of the nitrosochloride varied inversely as the rotation although the yield almost never exceeds 40 per cent of the theory. The crystalline nitrosochloride obtained is optically inactive and although a crystalline product can be obtained by first mixing strongly *d.* and *l.*pinenes, no crystalline product can be obtained by mixing the nitrosochloride solutions obtained by separately treating strongly rotatory *d.* and *l.*pinenes.[46] Tilden investigated the matter and concluded that the poor yield from pinene of high rotation is due to the destructive effects of the heat internally or locally generated in the reaction mixture.[47] Lynn[48] has recently succeeded in preparing optically active α-pinene nitrosochloride from the highly rotatory

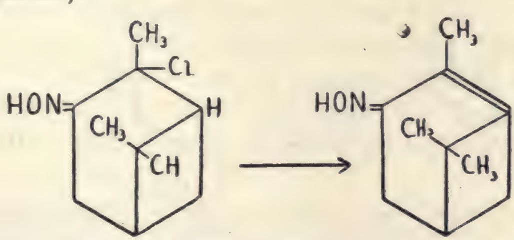
[44] *Compt. rend. 168,* 926 (1919).
[45] *Proc. Wisc. Pharm. Assoc. 1892,* 66.
[46] Gildemeister & Köhler, *Wallach Festschr. 1909,* 432.
[47] *J. Chem. Soc. 85,* 759 (1904).
[48] *J. Am. Chem. Soc. 41,* 361 (1919). For this purpose Lynn modified the usual method for preparing nitrosochlorides, using ethyl nitrite, absolute alcohol and alcoholic hydrogen chloride, the acid not being in excess.

d.α-pinene from the Port Orford cedar, previously described by Schorger, and also regenerated *d.α*-pinene from this nitrosochloride having a rotation of $[\alpha]_D + 53.75°$ (in 4 per cent alcoholic solution) which is the highest value yet reported and agrees well with the high value, $+ 51.52°$, previously reported by Schorger for the natural pinene from this cedar. The active nitrosochloride, $[\alpha]_D + 322°$, melts at 81°–81.5°, and is markedly soluble in all the common solvents, which probably accounts for the fact that it was not discovered earlier. The *d.*nitrolbenzylamine melts at 144°–145° and the nitrolpiperidine at 84°. Nevertheless, to account for the low yields of nitrosochloride Lynn suggests that the four-carbon ring may be broken to give 6-nitroso-8-chloro-Δ^1-p-menthene, or may react to give a product $C_{10}H_{15}NO + HCl$ in a manner similar to the reaction of nitrosyl chloride on n.heptane.[49]

When pinene nitrosochloride is treated with sodium methoxide, a methyl ether derivative is formed,[50] melting-point 102°, whose chemical behavior indicates the constitution,



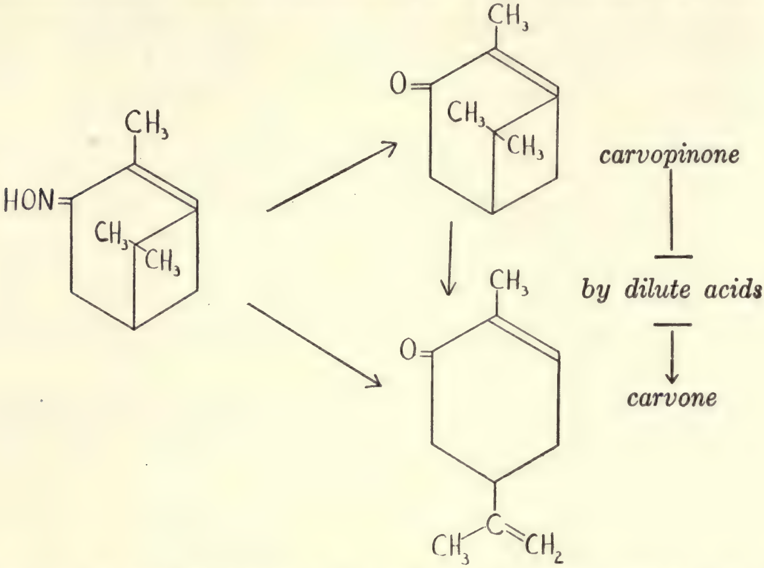
However, the chief result of the action of alcoholic caustic alkali on pinene nitrosochloride is the elimination of HCl in the usual way to form nitrosopinene,



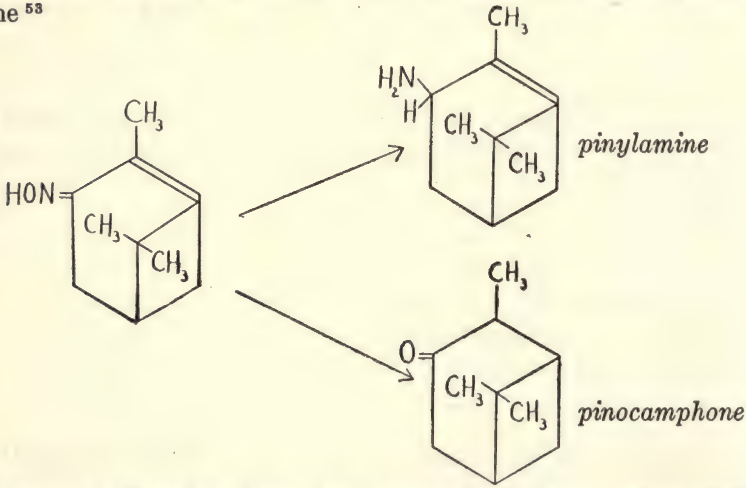
α-pinene nitrosochloride *nitrosopinene,* M.-P. 130°–131°

[49] Lynn, *J. Am. Chem. Soc. 41,* 367 (1919), finds that n.heptane reacts with NOCl in sunlight to give HCl, ammonium chloride and a mixture of heptanones.
[50] Deussen & Philipp, *Ann. 369,* 62 (1909); *374,* 112 (1910).

By warming with aqueous oxalic acid the *oxime* group is hydrolyzed to the ketone, carvopinone,[51] but in acetic acid solution with oxalic or hydrochloric acids the four-carbon ring is broken forming carvone.



By reduction with zinc dust and acetic acid nitrosopinene yields the unsaturated amine, pinylamine[52] and a saturated ketone, pinocamphone[53]

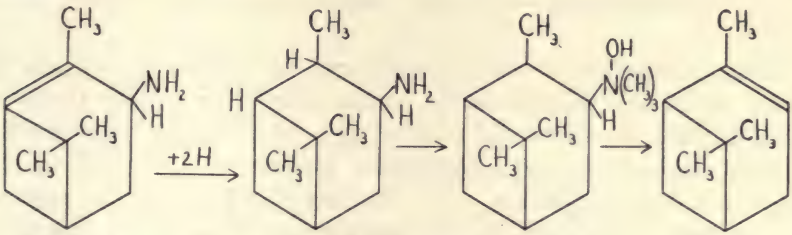


[51] Wallach, *Ann.* *346,* 231 (1906); boiling-point 94°-96° (12mm.), readily converted to carvone by heating with dilute acids.

[52] Wallach, *loc. cit.*; Pinylamine boils at 207°-208°, $d_{15°}$ 0.944. The nitrate is sparingly soluble in water which can be used for its recrystallization. The hydrochloride, melting-point 229°-230°, decomposes on heating to give ammonium chloride and cymene.

[53] Wallach, *346,* 235 (1906); *360,* 92 (1908); *389,* 185 (1912). The yield of pinocamphone by the reduction of nitrosopinene is about 22%. It boils at 211°-213° and

The first application of the method of exhaustive methylation of amines and their subsequent decomposition, which has been exceedingly useful in the study of the constitution of alkaloids, to the preparation of terpenes is the recent work of Ruzicka.[54] On hydrogenating pinylamine the saturated amine pinocamphylamine is formed, which on exhaustive methylation gives the trimethylpinocamphyl-ammonium hydroxide, the decomposition of which yields pure α-pinene, as follows,



pinylamine *pinocamphylamine* *trimethyl base* *α-pinene*

It is of interest to note that the four-carbon ring in pinocamphone is very much more stable to acids than the unsaturated ketone, carvopinone. The same stability is noted in the corresponding alcohol, pinocampheol,[55] made by the reduction of pinocamphone.

In general the halogen of alkyl halides[56] may be substituted by the triazo group, $-\mathrm{N}<\overset{\mathrm{N}}{\underset{\mathrm{N}}{||}}$. When α-pinene nitrosochloride is treated in alcoholic solution, with sodium azide, reaction takes place at about 40° to give a beautifully crystalline pinenenitrosoazide melting at 120°. Sodium ethoxide decomposes the azide to nitrosopinene. The chemical behavior of pinenenitrosoazide, and its physiological effect, is that of the aliphatic triazo derivatives in general. By heating with water the azide melting at 120° is partially isomerized to an azide melting at 126° and hot water alone breaks the four-carbon ring in the latter azide, losing nitrogen also, to form hydroxydihydrocarvoxime.[57]

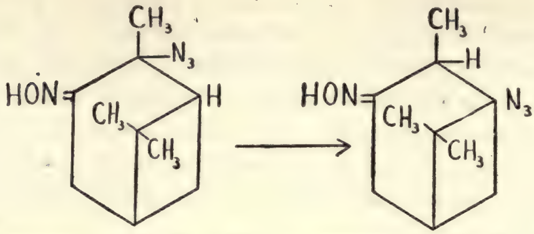
has a density of 0.959 (20). It yields an oxime melting at 86°-87° and a semicarbazone melting-point 208°. On oxidation it gives α-pinonic acid and an isomeric camphoric acid, $C_{10}H_{16}O_4$, melting at 186°-187°.

[54] Ruzicka & Trebler, *Helv. Chim. Acta.* *3*, 756 (1920).

[55] Wallach, *Ann.* *389*, 188 (1912).

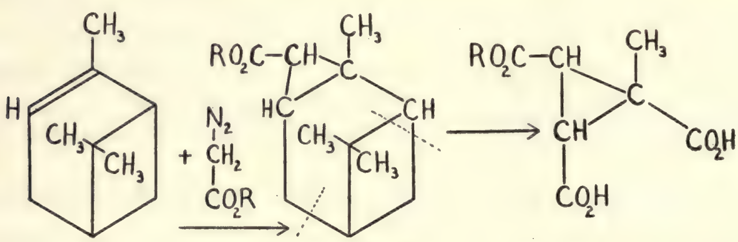
[56] Thus ethylenechlorohydrin reacts with NaN_3 to give triazoethyl alcohol. Vinyl bromide, which does not react with sodium azide, is an exception, which is another illustration of the stabilizing effect of an adjacent double bond upon a halogen atom.

[57] Forster & Newman, *J. Chem. Soc.* *99*, 245 (1911).



nitrosoazide, M.-P. 120° *nitrosoazide,* M.-P. 126°

When a solution of ethyl diazoacetate in a little *d.l.*α-pinene is slowly added to a mixture of the pinene and copper powder at 160°–165°, nitrogen is vigorously evolved and the resulting ester can be oxidized, through several intermediate products, to methylcyclopropane -1.2.3.-tricarboxylic acid. Buchner,[58] who has also applied this method to the study of the constitution of camphene and bornylene, considers that the results are best interpreted by Wagner's formula for α-pinene.



tricyclooctane derivative

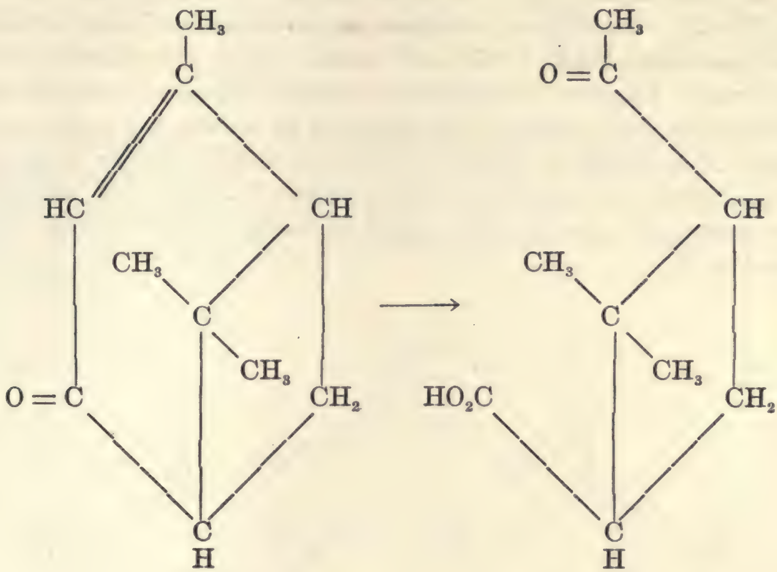
methylcyclopropane-1.2.3.-carboxylic acid

Bromine reacts energetically with α-pinene in cooled, dry carbon bisulfide to give a dibromide (reaction proceeds further with excess bromine, HBr being simultaneously evolved). When the crude dibromide is distilled with steam considerable decomposition occurs but one of the products is a crystalline dibromide, $C_{10}H_{16}Br_2$, of unknown constitution but which probably belongs to the camphor series.[59]

Verbenone: This ketone derivative of pinene was discovered in the

[58] *Ber. 46,* 2680 (1913). The trimethyltricyclooctanecarboxylic acid, noted above, melts at 165°.
[59] Wagner & Ginsberg, *Ber. 29,* 890 (1896).

essential oil of verbena[60] and has more recently been investigated by Blumann and Zeitschel, who found it in turpentine which had been considerably oxidized by the air.[61] It has a camphor and mint-like odor and its constitution was shown (by oxidation to pinononic acid, and other properties) to be as follows:



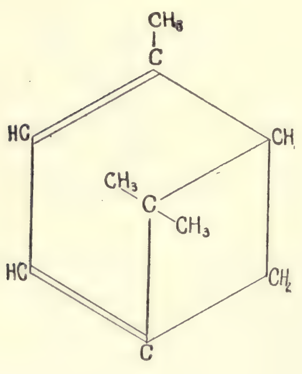
verbenone *pinononic acid*

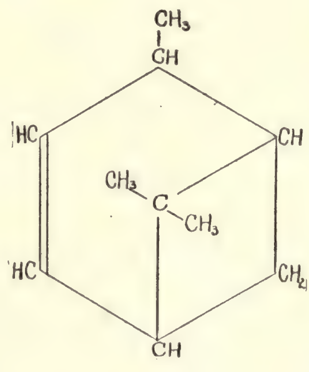
The fact that the double bond in pinene should apparently be preserved, may be explained by the initial hydration of the double bond, then oxidation of the CH_2 group and subsequent splitting off of water to form a double bond in the original position. Catalytic hydrogenation, using colloidal palladium, yields the saturated ketone, dihydroverbenone,[62] isomeric with pinocamphone.

The corresponding alcohol, *verbenol*,[63] also occurs in turpentine oxidized by air. The alcohol readily composes when distilled or when heated with acetic anhydride, forming verbenene, $C_{10}H_{14}$, which

[60] Kerschbaum, *Ber.* *33*, 885 (1900).
[61] *Ber.* *46*, 1178 (1913). Verbenone boils at 227°-228°, or 100° at 16mm. melts at 6.5, has a density of 0.9780 at 15° and $[\alpha]_D$ + 249.62°. Its oxime melts at 115°.
[62] Dihydro-d.verbenone, $C_{10}H_{16}O$, is an oil boiling at 222°, $d_{15°}$ 0.9685, semicarbazone melting at 220°-221° and oxime at 77°-78°.
[63] Boiling-point 216°-218°, $d_{15°}$ 0.9742.

hydrocarbon probably has two double bonds in a conjugated position as in α-terpinene. Dehydration of verbenol with phosphoric oxide or zinc chloride gave cymene. When *l*.verbenene, prepared from verbenol, is brominated in chloroform the crystalline dibromide, melting at 70°–72°, is formed. The *d*.dibromide from *d*.verbenene naturally melts at the same temperature but the racemic dibromide melts at 50°–52°. Oxidation of verbenene by permanganate yields norpinic acid melting at 175.5°–176.5°, and treatment with zinc chloride yields p-cymene. Blumann and Zeitschel[64] regard verbenene as having the constitution shown below, I; on reduction by sodium and alcohol two atoms of hydrogen are added (a reduction usually possible when the double bonds are conjugated) and the resulting hydrocarbon, dihydroverbenene or "δ-pinene" they regard as having the constitution indicated by II.





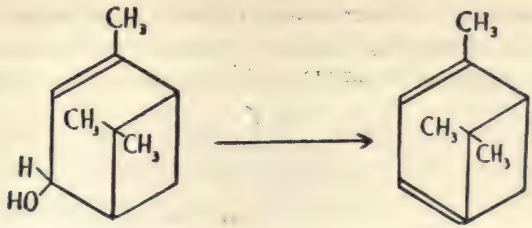
I. verbenene

$d_{15°}$	0.8867
$n\frac{20°}{D}$	1.4980
B.-P.	159°–160°

II. dihydroverbenene?

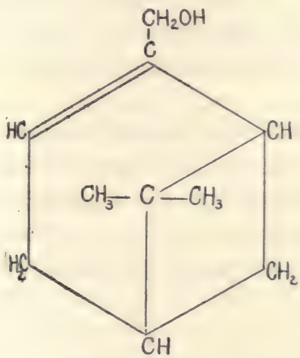
B.-P.	158°–159° (762 mm.)
$d_{20°}$	0.8625
$d\frac{20°}{D}$	1.4662

[64] *Ber.* 54, 887 (1921).



verbenol *verbenene ?*

An alcohol isomeric with verbenol and also possessing the bridged ring structure of pinene, is myrtenol, an alcohol occurring in myrtle oil as the acetate.[65] Its constitution is shown by the fact that reduction of the corresponding chloride by sodium and alcohol yields α-pinene.[66]



myrtenol

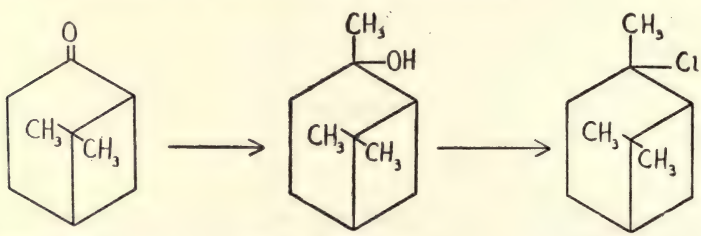
Oxidation by chromic acid yields the corresponding aldehyde myrtenal, but permanganate oxidizes it to *d*.pinic acid.

The *conversion of pinene to derivatives of borneol* is well known, the best example being the formation of bornyl chloride (so-called pinene hydrochloride) by the action of dry hydrogen chloride on

[65] Soden & Elze, *Chem. Ztg.* 29, 1031 (1905).
[66] Semmler & Bartelt, *Ber.* 40, 1363 (1907); myrtenol boils at 222°-224° (760mm.) or 102°-105° (9mm.).

pinene at about 15°. When bornyl chloride is prepared from pinene in the usual manner, the product is usually optically inactive but Barbier and Grignard[67] noted a rotation of $[\alpha]_D$ — 25.20° for the hydrochloride, melting-point 127°, made from *l.*-α-pinene from French turpentine, and a *d.*pinene hydrochloride (bornyl chloride), $[\alpha]_D$ + 33.19°, melting-point 127.1°, has been prepared[68] from *d.*α-pinene from Greek turpentine. The hydrochloride made by Lynn from highly active *d.*α-pinene from the Port Orford cedar was inactive, from which observations, together with many other observations of similar kind, it is evident that racemization occurs very readily, but under certain conditions, efficiency of cooling or rate of reaction, the activity may be partially preserved. In preparing limonene monohydrochloride partial racemization occurs, the degree of racemization apparently being influenced by the rate of introducing the hydrogen chloride, as shown by Vavon.[69] Pinene hydroiodide (bornyl iodide) was made by Aschan[70] by digesting bornyl chloride in ether with magnesium iodide; the iodide is easily reduced by zinc in acetic acid to camphane.

True pinene hydrochloride has not been detected among the reaction products of α-pinene and hydrogen chloride, but was synthesized by Wallach from nopinone by the Grignard reaction, thus making methylnopinol, and replacing the hydroxyl group in this alcohol by chlorine by means of phosphorus pentachloride,[71]



nopinone *methyl nopinol* *pinene hydrochloride*

[67] *Bull. soc. chim.* (4) *15,* 26 (1914).
[68] Tsakalotos, *J. pharm. chim.* *14,* 97 (1916).
[69] *Bull. soc. chim.* (4) *15,* 282 (1914).
[70] *Ber.* *45,* 2395 (1912); *d.* or *l.*pinene gives a hydroiodide melting at — 3° to — 5°; d.l.pinene gives the racemic hydroiodide melting at — 12°. Silver oxide in dilute alcohol converts the iodide into an evidently new unsaturated alcohol, $C_{10}H_{17}OH$, boiling-point 207°-211°.
[71] Wallach, *Ann.* *356,* 246 (1907).

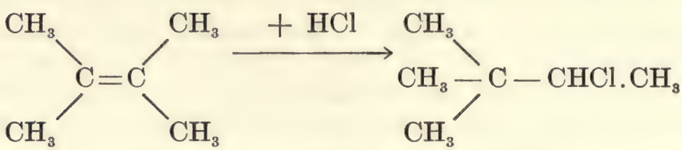
True pinene hydrochloride, as contrasted with bornyl chloride, is very unstable and decomposes at its boiling-point, 200°–205°, and is very readily converted to dipentene dihydrochloride by the action of hydrogen chloride; bornyl chloride is not affected by hydrogen chloride. By treating pinene dibromide with zinc in alcoholic solution a tricyclic hydrocarbon, melting at 65°–66°, is obtained. A diiodide, prepared by Frankforter and Poppe,[72] is very unstable, entirely losing its iodine merely on standing or by distilling a few times.

Anhydrous oxalic acid gives a relatively small yield of bornyl esters, dipentene and terpinenes being the chief products (see Artificial Camphor). Acetic acid at 200° also gives a certain amount of bornyl acetate.[73] The oxalic acid reaction was the basis of the first industrial process for the manufacture of artificial camphor.

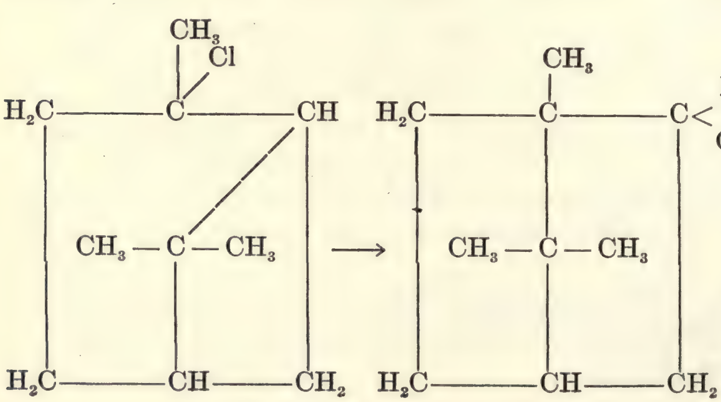
When pinene is treated with HCl in the presence of moisture, or at too high temperatures, oily mixtures are obtained, the chief product being dipentene dihydrochloride. Under the best conditions the yield of crystalline bornyl chloride does not exceed 75 to 78 per cent of the theory. The liquid, oily chloride mixture contains bornyl chloride in solution, also dipentene dihydrochloride and lesser amounts of other substances. Barbier and Grignard[74] have investigated these hydrochloride oils, converting these hydrochloride oils into the magnesium compounds and treating the latter with oxygen and also with carbon dioxide. In addition to bornyl chloride, they found indications of the presence of fenchyl chloride. Aschan[75] has carefully investigated these oily hydrochlorides, having at his disposal comparatively large quantities of material made incidental to the manufacture of artificial camphor. By the action of alkali on the chlorides he obtained a complex mixture of hydrocarbons and showed that the low-boiling fraction contained (1) *d.l.*bornylene (which yields *d.l.*camphoric acid on oxidation), (2) a bicyclic hydrocarbon boiling at 144°–145° which he called α-pinolene, and (3), a tricyclic hydrocarbon, boiling-point 143°, which was quite stable to permanganate and which he named β-*pinolene* or tricyclene. This hydrocarbon, which has been obtained as one of the products of the decomposition of fenchyl chloride by Aschan[76] and by Sandelin,[77] is probably identical with the *cyclofenchene* of Quist.[78]

[72] *J. Am. Chem. Soc. 28,* 1461 (1906).
[73] Austerweil, *Compt. rend. 148,* 1197 (1909).
[74] *Bull. soc. chim.* (4) 7, 342 (1916).
[75] *Ber. 40,* 2750 (1907); *Ann. 387,* 27 (1912).
[76] *Ann. 387,* 27 (1912).
[77] *Ann. 396,* 297 (1913).
[78] *Ann. 417,* 278 (1918).

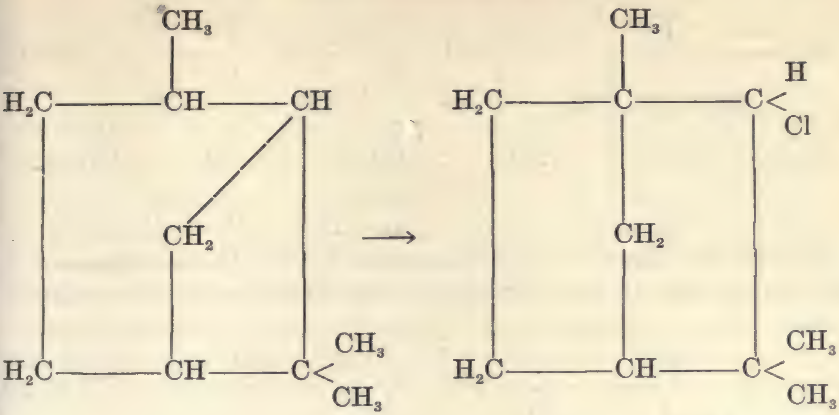
By decomposing fenchyl alcohol by heating with potassium acid sulfate, Quist obtained two hydrocarbons, one being the low-boiling "cyclofenchene" or β-pinolene. Fenchyl alcohol cannot decompose to water and an unsaturated hydrocarbon, forming a double bond with an *adjacent* carbon atom, as will be evident from its constitution. Other hydrocarbons may be formed from β-pinolene by rearrangement. Quist confirms Aschan as to its stability to permanganate but discovered that the three-carbon ring is evidently broken by the addition of bromine, forming a well crystalline dibromide of unknown constitution. The chemistry of the fenchenes (q.v.) into which these derivatives of pinene lead, is still in a very unsettled condition. As regards their formation from α-pinene Aschan recalls that when hydrogen chloride reacts with tetramethyl ethylene, a rearrangement occurs.



which is analogous to the addition of HCl to pinene, and if we recall that the CH_2 and $>C<\begin{matrix}CH_3\\CH_3\end{matrix}$ groups in the four-carbon ring are equivalent as regards their spatial relations to the rest of the molecule, we may write the rearrangement of the initial hydrochloride as follows,

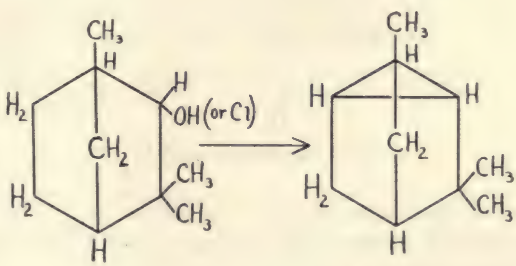


bornyl chloride



chloride of fenchyl alcohol

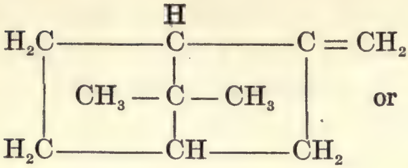
According to Aschan and Quist the formation of β-pinolene (cyclofenchene), from fenchyl alcohol or fenchyl chloride is to be expressed as follows,



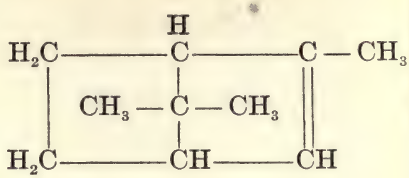
fenchyl alcohol *β-pinolene*

Isopinene is the name given by Aschan [79] to a hydrocarbon, boiling-point 154.5°–155.5°, d_{20° 0.8658, n_D 1.47025, obtained by reacting upon β-pinolene with hydrogen chloride and then decomposing the hydrochloride with aniline. Aschan identified *cis*-apocamphoric acid among the oxidation products of iso-pinene. Aschan reasons that isopinene, barring rearrangements, can have only structure I or II

[79] *Chem. Zentr. 1909* (2), 26.

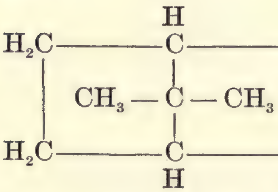


or

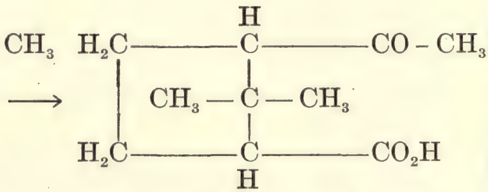


I *II*

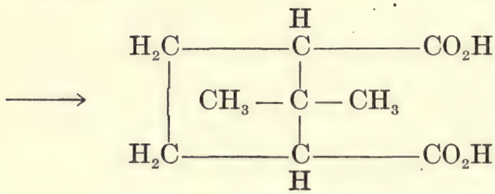
Wallach considers that *d.l.*fenchene has the constitution represented by I, and also II best accounts for the formation of apocamphoric acid.



isopinene

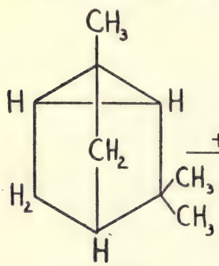


fenchenonic acid

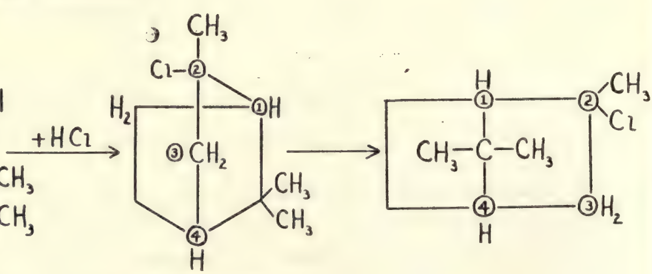


apocamphoric acid

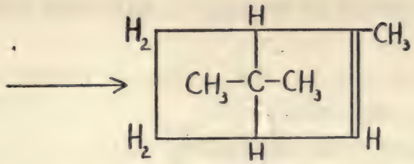
The formation of isopinene by the rupture of the three-carbon ring in β-pinolene and the subsequent removal of HCl may be understood by the following reactions,



β-*pinolene*
B.-P. 142°–144°

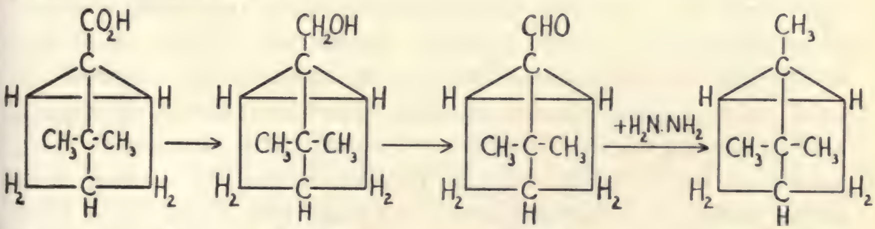


β-*pinolene*
hydrochloride
M.-P. 26°



isopinene

Tricyclen: When camphene is treated with nitrous acid, camphenylnitrite, $C_{10}H_{15}NO_2$, is formed[80] and when this derivative is treated with concentrated sulfuric acid, with good cooling an excellent yield of tricyclenic acid is obtained.[81] Its constitution has been shown by Komppa[82] to be as shown below. Attempts to oxidize tricyclenic acid or the hydrocarbon tricyclene by permanganate to a cyclopropanetricarboxylic acid, as Buchner and Weigard have done in the case of the condensation product of bornylene (q.v.) and diazoacetic ester, was without definite result[83] but the three-carbon ring in ω-aminotricyclene is split by concentrated hydrochloric acid to form camphenilane aldehyde and ammonium chloride. The ester of tricyclenic acid can be reduced by the method of Bouveault and Blanc to "tricyclol" and the latter can be oxidized by chromic acid in acetic acid solution, without breaking the three-carbon ring, to the corresponding aldehyde. This aldehyde is readily converted by the hydrazine method of Kishner[84] and Wolff[85] to *tricyclene*, the yield being practically quantitative.[86]



tricyclenic acid *tricyclal* *tricyclol* *tricyclene*

Pure tricyclene (Lipp) boils at 151.6°–152° and melts at 64°–65°.[87] Tricyclene is unchanged by boiling (in benzene) with zinc chloride

[80] Jagelkische, *Ber. 32,* 1501 (1902).
[81] Bredt & May, *Chem. Ztg. 1909,* 1265.
[82] *Ber. 41,* 2747 (1908); *44,* 1536 (1911).
[83] Komppa, *loc. cit.* Lipp, *Ber. 53,* 771 (1920).
[84] *Chem. Zentr. 1911* (2) 363, 1925.
[85] *Ann. 394,* 86 (1912).
[86] Lipp, *Ber. 53,* 772 (1920); tricyclol melts at 111°-112° and tricyclal melts at 85°-90° (semicarbazone 219°-220°).
[87] Moycho & Zienkowski, *Ann. 340,* 24 (1905), give M.-P. 67.5°-68°, B.-P. 152°-152.8°. Eijkman (*Chem. Zentr. 1907* [2], 1210), gives M.-P. 66.5°, B.-P. 152.5°. Roth & Ostling (*Ber. 46,* 312 [1913]), gives M.-P. 62.5°-63°, B.-P. 152°.

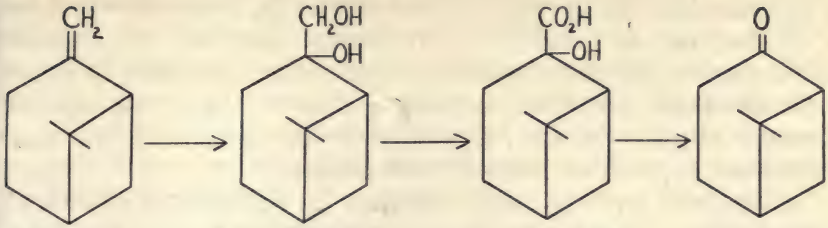
but is converted to camphene by heating to 160° with sodium bisulfate.

Tricyclene is also formed by the action of mercuric oxide on camphor hydrazone (*v.* camphene).

When tricyclene reacts with chloroacetic acid, an ester of camphene hydrate is first formed.[88] This and other evidence indicates that the three-carbon ring is easiest broken between carbon atoms 1 and 2 or 1 and 6. Thus tricyclene yields isocamphane [89] when hydrogenated over catalytic nickel at 180°, but when passed over nickel at 180° without adding hydrogen, tricyclene is isomerized to camphene. Bromine yields a liquid dibromide of unknown constitution. Hydrogen chloride passed into a cold ethereal solution of tricyclene forms a well crystalline hydrochloride melting at 125°–127° and camphene yields the same hydrochloride under the same conditions. Meerwein regards this chloride as the true camphene hydrochloride corresponding to Aschan's camphene hydrate. This hydrochloride decomposes on standing at room temperature, recalling the similar behavior of chlorinated gasoline and kerosene hydrocarbons (of unknown constitution). Free hydrogen chloride, particularly in alcohol solution, accelerates the change of this chloride to isobornyl chloride, melting-point 158°.

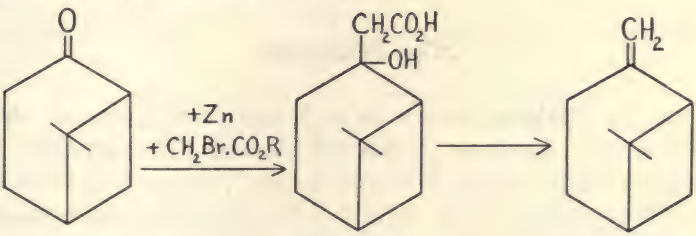
Beta-pinene is a constituent of commercial American and French turpentine and, according to Vavon,[90] American turpentine contains about 27 per cent of this terpene. Baeyer and Villiger discovered the sparingly soluble nopinic acid by the oxidation of turpentine by cold, alkaline permanganate solution. Further oxidation of nopinic acid by heating with lead peroxide (in water) yields nopinone.[91] This ketone is converted to 4-isopropylcyclohexenone by heating with dilute acids. The constitutions of nopinone and nopinic acid have been shown to be those suggested by Baeyer. The oxidation of β-pinene by the customary reactions proceeds normally. The yields of the various oxidation products are small but nopinic acid can be isolated without great difficulty. Small proportions of β-pinene can thus be detected with certainty.

[88] Meerwein, *Ber.* *53*, 1820 (1920).
[89] Lipp, *Ann.* *382*, 265 (1911).
[90] *Compt. rend.* *149*, 997 (1909).
[91] *Ber.* *29*, 25, 1923 (1896). The oxime of nopinone is an oil, but the semicarbazone melts at 188.5°; nitric acid oxidizes nopinone to homoterpenylic acid.



β-pinene *β-pineneglycol* M.-P. 75°–77° *nopinic acid* M.-P. 126° *nopinone*

By the use of Reformatsky's reaction, condensation with bromoacetic ester by zinc, Wallach made the nopinol acetic acid which decomposes with loss of water and CO_2 in two ways according to the conditions employed. By heating with acetic anhydride β-pinene and an acid melting at 85°–86° is obtained. Wallach[92] represents the synthesis of β-pinene as follows,



nopinone *nopinolacetic acid* *β-pinene*

Reduction of nopinone gives the corresponding alcohol, nopinol, in two modifications, a crystal form melting at 102° and a liquid form. By the Grignard reaction methylnopinol (pinene hydrate), crystals melting at 58°–59°, and ethylnopinol, melting-point 43°–45°, have been prepared. Methylnopinol is readily changed by five per cent sulfuric acid to α-terpineol, but nopinol is stable to dilute acid, illustrating again the influence of changes in other parts of the molecule upon the stability of the four-carbon ring in the pinenes. Hydration also gives *cis*-terpin hydrate, melting at 117°. Heating nopinone with dilute sulfuric acid gives 4-isopropyl-Δ^2-cyclohexenone.[93]

Hydrogenation of β-pinene gives pinane identical with that derived by the hydrogenation of α-pinene.[94] β-pinene does not form a nitro-

[92] *Ann.* *363*, 9 (1908); *368*, 7 (1909); *356*, 231 (1907). Nopinone melts at about 0°, boils at 209°; nopinol acetic acid melts at 85°-86°.
[93] Rimini, *Gazz. chim. Ital.* *46* (2), 119 (1916).
[94] Vavon, *Compt. rend.* *150*, 1127 (1910).

sochloride, but nitrous acid yields a nitroso-β-pinene discovered by Pesci and Bettelli[95] and which Wallach showed was characteristic for β-pinene. When turpentine is hydrated by dissolving in acetic acid and acetic anhydride and adding a little 50 per cent aqueous benzene-sulfonic acid, the β-pinene reacts first, which behavior may be utilized in purifying α-pinene from β-pinene.[96]

Fairly pure β-pinene can be obtained by fractional distillation of the terpenes in hyssop oil, taking advantage of the fact that β-pinene boils approximately 10° higher than ordinary pinene; β-pinene from this source showed, boiling-point 164°–166° d_{15° 0.8650, $n\frac{20^\circ}{D}$ 1.47548. Wallach's synthetic β-pinene showed boiling-point 163°–164° d_{22° 0.8675, $[\alpha]_D$ —25° 5′, $n\frac{22^\circ}{D}$ 1.4749.

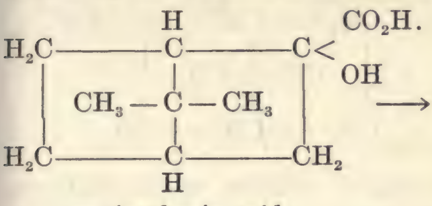
The Fenchenes.

Three hydrocarbons, known as α, β and γ-fenchenes, are derived from the ketone fenchone or fenchyl alcohol. The fenchenes have not been positively identified in any natural product and their structure has been arrived at by reference to the parent substances and, more recently, by methods of synthesis. Like the chemistry of camphene and bornylene, the chemistry of the fenchenes has only recently been made clear, although the nature of the puzzling rearrangements shown to occur in this series, are far from being understood. The current literature contains a great deal of work on these derivatives but the constitutions of the principal members of the group appear to be definitely determined.

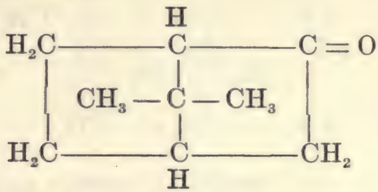
Fenchone: This ketone closely resembles camphor in its chemical behavior but is more resistant to oxidizing agents. It can accordingly be purified from other substances by oxidizing the impurities with concentrated nitric acid or by permanganate and can also be prepared readily by oxidizing the corresponding alcohol, fenchyl alcohol, which occurs in old root wood of the yellow pine, *Pinus palustris*, and is therefore a constituent of wood turpentine distilled from old stump wood. *d.*-Fenchone occurs in fennel oils and *l.*fen-

[95] *Gazz. chim. Ital. 16*, 337 (1886); Wallach, *Ann. 346*, 246 (1906).
[96] Barbier & Grignard, *Bull. soc. chim.* (4) *3*, 139 (1908); *5*, 512, 519 (1909).

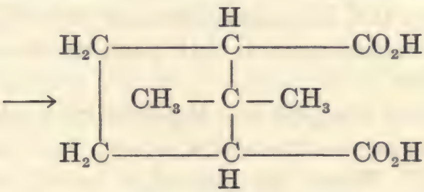
chone in thuja oils.[97] Fenchone does not form a hydroxymethylene derivative, indicating the absence of a $—CH_2—CO—$ group. By converting fenchyl alcohol to the chloride and decomposing the fenchyl chloride by heating with aniline, "fenchene" was produced. By oxidizing this unsaturated hydrocarbon by permanganate oxyfenchenic acid is formed which may be further oxidized to fenchocamphorone. As a result of a detailed study of these products and the known properties of fenchone Wallach [98] proposed the constitutions shown below for these substances, the correctness of which was soon proven by their oxidation to apocamphoric acid.[99]



oxyfenchenic acid

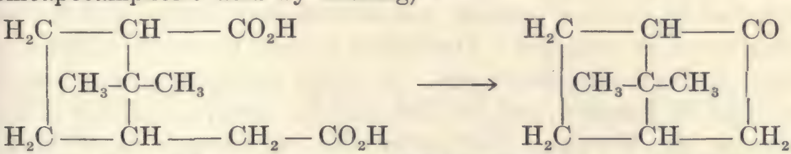


fenchocamphorone



apocamphoric acid

Wallach's constitution for fenchocamphorone is also confirmed by its synthesis in a very direct manner, by decomposing the lead salt of homoapocamphoric acid by heating,[100]



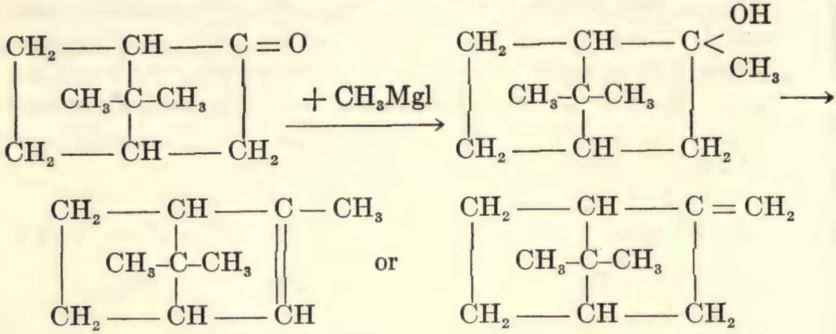
[97] Fenchone melts at 5° to 6°. The physical properties of a specimen regenerated from the semicarbazone [Wallach, *Ann.* *362*, 195 (1908)] were as follows, boiling-point 192°-193°, $d_{18°}$ 0.948, $[\alpha]_D + 62.76°$ (higher in alcohol solution) $n_D^{18°}$ 1.46355. Fenchone does not form a phenylhydrazone but readily gives an oxime, *d.* and *l.* melting at 164°-165°, inactive form melting at 158°-160° [Wallach, *Ann.* *272*, 104 (1893)]. The semicarbazone forms very slowly; Wallach recommends allowing an alcoholic solution of the ketone, semicarbazid hydrochloride and sodium acetate to stand for two weeks [*Ann.* *353*, 211 (1907)]. The semicarbazone crystallizes from dilute alcohol in long prisms melting at 182°-183°.

[98] *Ann.* *300*, 320.

[99] *Ann.* *315*, 293 (1901).

[100] Komppa, *Ber.* *44*, 395 (1911). The racemic semicarbazone of fenchocamphorone melts at 220°.

By reacting upon α-fenchocamphorone with methyl magnesium iodide Komppa and Roschier[101] have synthesized-α-fenchene. The tertiary alcohol formed by this reaction is decomposed by distilling at ordinary atmospheric pressure to give the hydrocarbon.



The physical properties and chemical behavior of the synthetic α-fenchene[102] are practically identical with Aschan's isopinene (q.v.), but Wallach considers that α-fenchene contains the $>C=CH_2$ group, on account of its formation together with β-pinene when nopinolacetic acid is dehydrated.[103]

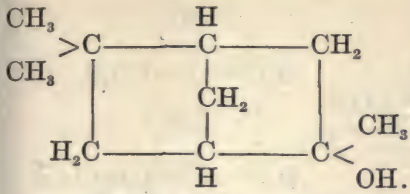
In a similar manner Komppa and Roschier have treated *d.l.*β-fenchocamphorone with magnesium-methyl iodide, thus forming methyl-β-fenchocamphorol.[104] When this alcohol is heated with potassium acid sulfate a mixture of two unsaturated hydrocarbons is obtained, consisting mainly of *d.l.*β-fenchene and an endocyclic hydrocarbon γ-fenchene. The β hydrocarbon yields *d.l.* hydroxy-β-fenchenic acid melting at 124°–125° on oxidizing with permanganate, and on further oxidation by the lead peroxide and sulfuric acid method *d.l.*β-fenchocamphorone is obtained. The latter ketone by further oxidation yields apofenchocamphoric acid. A fourth fenchene, termed isoallofenchene by Semmler, and isofenchylene by Quist, is called δ or isofenchene by Komppa. The β-fenchene of Komppa is Wallach's D, *d.* or L. *l.* fenchene, or Semmler's isofenchene.

[101] *J. Chem. Soc.* **112** (1), 466 (1917).

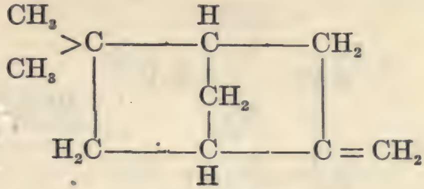
[102] The synthetic hydrocarbon of Komppa boils at 154°-156°, has a density $\frac{20°}{4°}$ 0.8660 and refractive index $\frac{20°}{D}$ 1.47045. The hydrochloride, melting-point 35°-37° is identical with that made from isopinene. Ozone gives racemic fenchocamphorone and r α-fenchenylanic acid, melting-point 105°.

[103] *Ann.* *363,* 3 (1908).

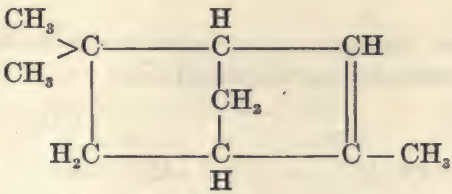
[104] *Chem. Abs.* *13,* 2864 (1919). Fenchocamphorol melts at 66°-67° and boils at 77° (9mm.); ν-fenchene boils at 146°-148°, d $\frac{20°}{4°}$ 0.8539.



methyl-β-fenchocamphorol



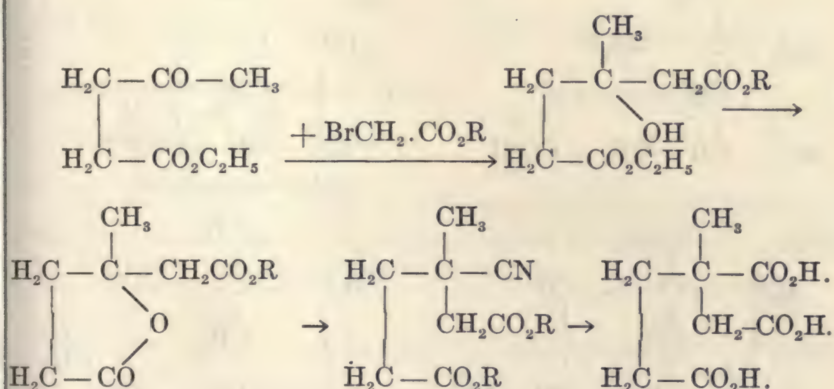
β-fenchene



γ-fenchene

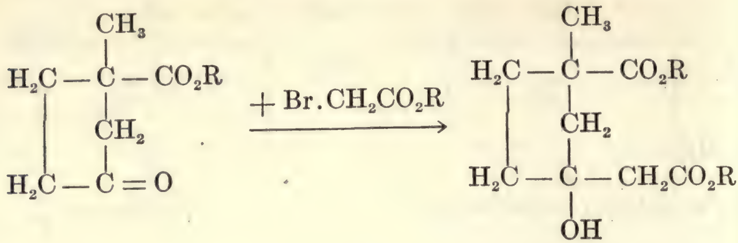
Fenchone itself has been synthesized by Ruzicka [105] in the manner indicated by the following reactions.

(1) Levulinic ester and ethyl bromoacetate are condensed by means of zinc and the resulting lactonic ester is converted into the nitrile by treating with potassium cyanide,

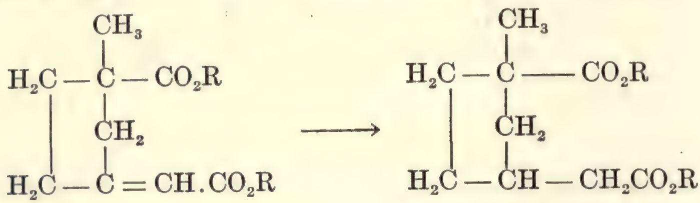


(2) The above tricarboxylic acid is condensed to a cyclopentanone derivative by means of sodium in benzene, and the ester of the resulting product is condensed with bromoacetic ester.

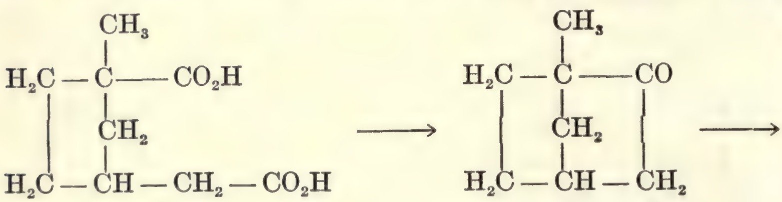
[105] *Ber.* 50, 1362 (1917).



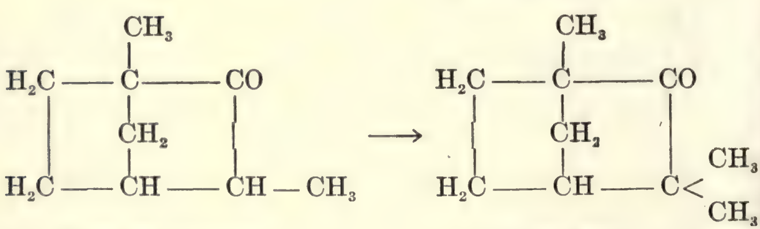
(3) The above hydroxy acid is converted to the unsaturated acid and the latter reduced to the saturated acid.



(4) On heating the lead salt of the above acid methylnorcamphor is formed which on methylating by Haller's method, using sodium amide and methyl iodide, fenchone and fenchosantenone are formed.



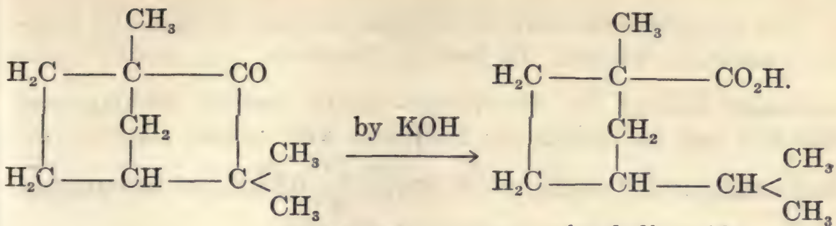
methylnorcamphor



fenchosantenone *fenchone*

The above structure of fenchone explains the formation of fencholic acid from fenchone by heating with caustic potash.[106]

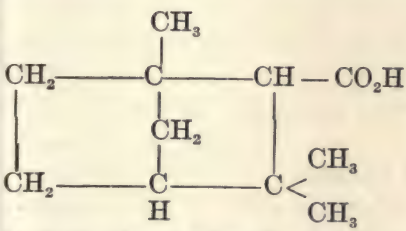
[106] Wallach, *Ann.* **369**, 71 (1909).



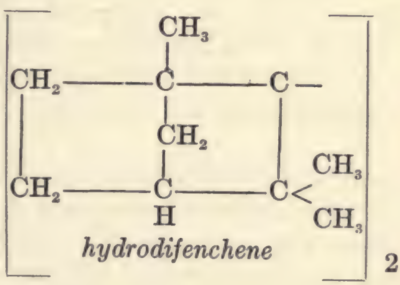
fencholic acid

By the action of sodium or potassium acid sulfates on fenchyl alcohol at 170°–180°, in a current of carbon dioxide, a fenchene is obtained boiling at 151°–153°, D 0.8660. On oxidation it yields hydroxyfenchenic acid melting at 138°–139°.[107]

Fenchyl chloride, like the higher alkyl halides in general, reacts very slowly with magnesium in ether. After one week and treating with carbon dioxide the reaction mixture gives chiefly hydrofenchene carboxylic acid and hydrodifenchene.[108]

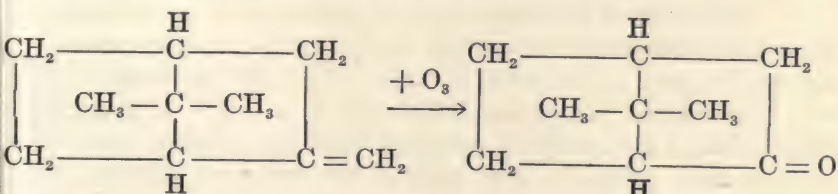


hydrofenchenecarboxylic acid
M.-P. 45°–46°
(racemic acid M.-P. 52°–53°)



hydrodifenchene

By the action of ozone on α-fenchene Komppa and Hintikka [109] obtained fenchocamphorone, which behavior is also readily explained by Wallach's formula for this hydrocarbon.



[107] *J. Chem. Soc.* *112*, 398 (1917).
[108] Komppa & Hintikka, *Ber.* *46*, 645 (1913).
[109] *Ber.* *47*, 936 (1914).

The saturated hydrocarbon, fenchane, has been prepared by Kishner's admirable method. By heating *d*.fenchone, $[\alpha]_D + 62.8°$, with hydrazine hydrate the *d*.hydrazone is first formed (melting-point 56°–57°) and by heating the hydrazone with sodium ethylate fenchane is formed,[110] boiling-point 149°, $d\frac{20°}{4°}$ 0.8316 and lævorotatory $[\alpha]_D - 18.11°$ (4 per cent solution in alcohol).

[110] Wolff, *Ann.* *394*, 86 (1912).

Chapter XIII. Bicyclic Non-benzenoid Hydrocarbons.

Camphene and Bornylene.

Although these two hydrocarbons have quite different structures they are considered together on account of their relations with pinene and bornyl halides, and with borneol and camphor. Until recent years the existence of bornylene, as distinguished from camphene, was not recognized. The chemistry of these two hydrocarbons, particularly that of camphene and its oxidation products, is somewhat involved but by 1914 the accumulation of evidence was such that the constitution of these two hydrocarbons could be considered as established beyond any reasonable doubt. Particularly is this true since the synthesis of camphenic acid by Lipp [1] and the investigations of Haworth and King.[2]

Camphene and bornylene are both solid and crystalline at ordinary temperatures, but only camphene has been found in nature, occurring in both *d.* and *l.* forms. Camphene was early recognized as a product of the decomposition of bornyl chloride, the *l.*chloride giving *l.* camphene and the *d.*chloride giving *d.* camphene.[3]

Although camphene crystallizes well and purification by recrystallization has been carried out in most cases, the physical properties reported for camphene are far from being in agreement. The differences noted in physical properties are doubtless due to the presence of bornylene or to some other as yet unidentified hydrocarbon.

When borneol derivatives are decomposed to hydrocarbon under milder conditions the chief product is bornylene, a hydrocarbon first recognized by Wagner.[4] Bornyl iodide, made from borneol and hydriodic acid (which is identical with the product of HI and pinene), gives mainly bornylene on treating with alcoholic caustic alkali.

[1] *Ber. 47,* 871 (1914).
[2] *J. Chem. Soc. 105,* 1342 (1914).
[3] Berthelot, *Ann. 10,* 367 (1859); Kachler, *Ann. 179,* 96 (1879); Tilden & Armstrong, *Ber. 12,* 1753 (1879).
[4] *Ber. 32,* 2302 (1899).

PHYSICAL PROPERTIES OF CAMPHENE.

Source	*M.-P.*	*B.-P.*	*Density*	$[\alpha]_D$	n_D
Sibirian pine needle[1]	39. °	160. °–161. °	0.8555 (40°)	−84.9 °	1.46207(40°)
Pinene, Am. turpentine[2]	43. °–43.5°	158. °–158.5°	0.8486 $\left(\frac{50°}{4°}\right)$	+17.95°	1.46048(50°)
Pinene, Greek turpentine[3]	46. °–47. °	157.2°–157.9°	0.8446 $\left(\frac{50°}{4°}\right)$	+74.55°	1.4561 (50°)
Borneol, thru chloride[3]	48. °–49. °	160. °–161. °	0.850 (48°)	......	....
" " "[4]	53.5°–54. °	....	0.83808 $\left(\frac{58°}{4°}\right)$	......	1.4531 (58°)
Pinene, thru hydrochloride[5]	51. °–52. °	158.5°–159.5°	0.8422 $\left(\frac{54°}{4°}\right)$	......	1.4551 (54°)
Isoborneol, dehydration	50. °	159. °–160. °	.....	......	....

1 Wallach, *Ann. 537*, 79 (1907).
2 Aschan, *Ann. 398*, 299 (1913).
3 Wallach, *Ann. 230*, 234 (1885).
4 Brühl, *Ber. 25*, 164 (1892).
5 Bertram, Wahlbaum, *J. prakt. Chem.* (2) *49*, 8 (1894).

Also when borneol xanthogenate is heated it decomposes to give chiefly bornylene, a method discovered by Tschugaeff.[5] Henderson and Caw[6] showed that when bornylene is prepared by Tschugaeff's method, the impurities can be removed by oxidizing with hydrogen peroxide, the bornylene so purified melting at 113°, and boiling at 146°–147° (750 mm.). Bornylene has recently been made from camphor by Ruzicka[7] by the conversion of camphor to bornylamine by heating with ammonium formate in an autoclave at 60 atmospheres pressure; the resulting amine was subjected to the method of exhaustive methylation with methyl iodide (bornyltrimethylammonium iodide melts at 245°). The free trimethyl base is gently decomposed to give bornylene melting-point 111°–112°.

Bredt has also made a very pure bornylene from camphocarboxylic acid. By *electrolytic reduction* of this acid to the corresponding hydroxy acids[8] and distilling the acetylborneolcarboxylic acid the unsaturated acid, bornylenecarboxylic acid,[9] is obtained and on reacting upon this acid with hydrogen bromide a mixture of α and β-bromocamphanecarboxylic acids are obtained. The β-bromo acid is decomposed on heating with aqueous alkali to bornylene, bornylenecarboxylic acid and a lactone.

$$C_8H_{14}<\begin{array}{l}CH.CO_2H\\ |\\ C=O\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH.CO_2H\\ |\\ CH.OH.\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C-CO_2H.\\ \|\\ CH\end{array} \xrightarrow{+\ HBr}$$

$$\longrightarrow C_8H_{14}<\begin{array}{l}CH.CO_2H\\ |\\ CHBr\end{array} \quad \text{and} \quad C_8H_{14}<\begin{array}{l}CBr.CO_2H.\\ |\\ CH_2\end{array}$$

β-bromocamphene-carboxylic acid.

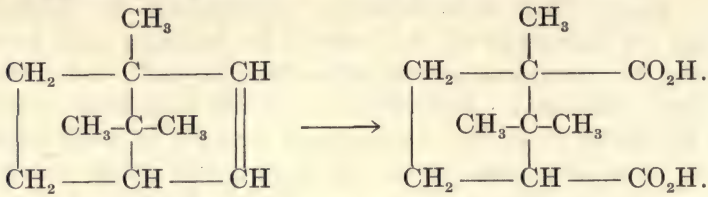
$$\searrow \quad C_8H_{14}<\begin{array}{l}CH\\ \|\\ CH.\end{array} \quad \text{bornylene}$$

The bornylene thus obtained had the following physical properties, melting-point 113°, boiling-point 146° (740 mm.), $[\alpha]_D$ —21.69° (10.4% in toluene), $[\alpha]_D$ —26.96° (4.42% in methyl alcohol).

Bornylene gives camphoric acid on oxidation, which indicates that

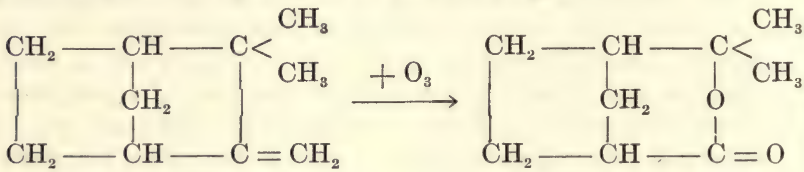
[5] Tschugaeff & Budrick, *Ann. 388*, 280 (1912).
[6] *J. Chem. Soc. 103*, 1543 (1912).
[7] *Helv. chim. Acta. 3*, 48 (1920).
[8] Bredt, *Ann. 366*, 1 (1909). These are *cis* and *cis-trans* isomeric forms of borneolcarboxylic acid, the *cis* acid melting at 102°-103° and the *cis-trans* melting at 171°.
[9] Melting-point 112°-113°, boiling-point 158° at 13mm.

the double bond is in the position shown, which structure is that formerly supposed to represent the constitution of camphene,



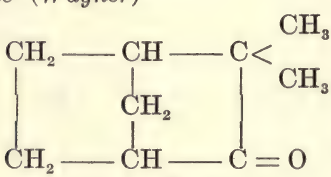
bornylene *camphoric acid*

Camphene forms an ozonide which on decomposition gives formaldehyde-camphenilone and dimethylnorcampholide.[10] Komppa and Hintikka [11] have synthesized the latter substance and shown its constitution to be as represented in the following.



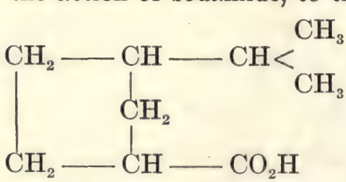
camphene (Wagner) *dimethylnorcampholide*

and



camphenilone

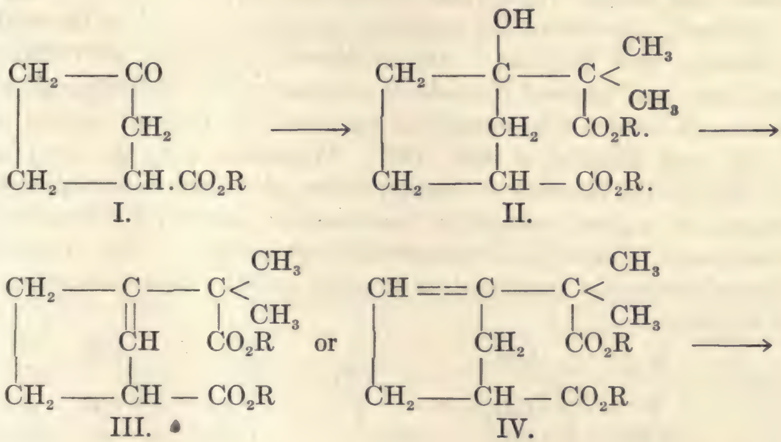
This constitution of camphenilone is supported by the fact that it does not form a hydroxymethylene compound [12] and therefore does not possess a CH_2 group adjacent to the carbonyl group. Further evidence of the structure of camphenilone is given by the conversion of camphenilone by the action of sodamide, to the amide of the acid,

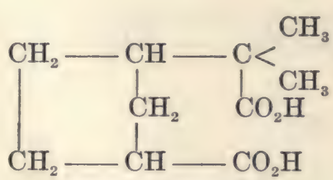


which substance has also been synthesized.[13]

[10] Harries & Palmen, *Ber. 43,* 1432 (1910).
[11] *Ber. 42,* 898 (1909).
[12] Moycho & Zienkowski, *Ann. 340,* 54 (1905).
[13] Bouveault & Blanc, *Compt. rend. 147,* 1314 (1908).

When camphene is oxidized by alkaline permanganate the chief product is camphenic acid, $C_{10}H_{16}O_4$, an acid isomeric with camphoric acid. A great deal of work has been done upon the structure of this acid, based upon which other constitutions for camphene have been proposed.[14] However no reasonable doubt should exist as to its constitution since its synthesis by Lipp,[15] in the following manner: The ethyl ester of 1.3-cyclopentanonecarboxylic acid was condensed, by Reformatsky's reaction, with α-bromoisobutyric ester in the presence of zinc. By decomposition with loss of water an unsaturated acid was formed, whose constitution may be either III or IV but on hydrogenating the saturated acid 1.3-carboxylcyclopentylisobutyric acid was formed, which proved to be identical with *d.l.cis*-camphenic acid.[16]



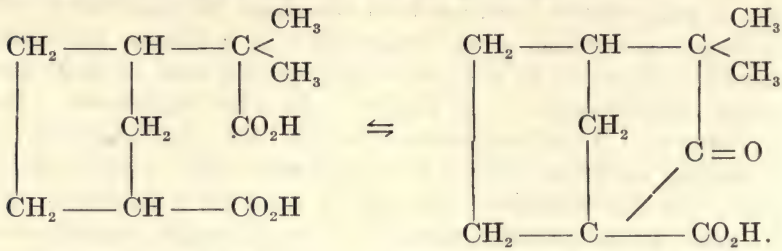


camphenic acid

When camphenic acid is distilled it loses CO_2 to form a ketonic acid, camphenonic acid, whose constitution may be inferred from the structure of camphenic acid. The *d.* and *l.* forms of camphenonic

[14] Cf. review by Haworth & King, *J. Chem. Soc. 101,* 1975 (1912).
[15] *Ber.* 47, 871 (1914)
[16] Camphenic acid is practically insoluble in cold water, ligroin and carbon bisulfide, but crystallizes from hot water, melting-point 135°-137°.

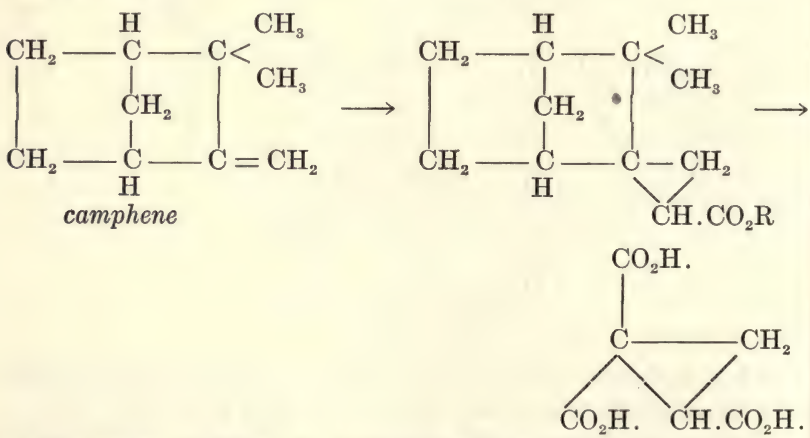
acid together with the *d.l.* acid are formed from camphenic acid made by the oxidation of strongly *d.* or *l.* camphene.[17]



camphenic acid *camphenonic acid.*

Fusion of camphenonic acid with caustic alkali or treatment with sodium and alcohol regenerates camphenic acid.

Wagner's constitution for camphene is also supported by the work of Buchner and Weigand,[18] who condensed camphene with diazoacetic ester and oxidized the acid so obtained to 1.1.2-cyclopropanetricarboxylic acid. The camphene employed by Buchner melted at 44°–45° and distilled at 156°–157°. Treatment with the ester at 160°–165° in the presence of copper powder gave vigorous evolution of nitrogen and a good yield of the condensation product, 2.2-dimethylnorcamphane-3-spirocyclopropanemethylcarboxylate. The relation of camphene to the condensation product and the oxidation product are as follows:



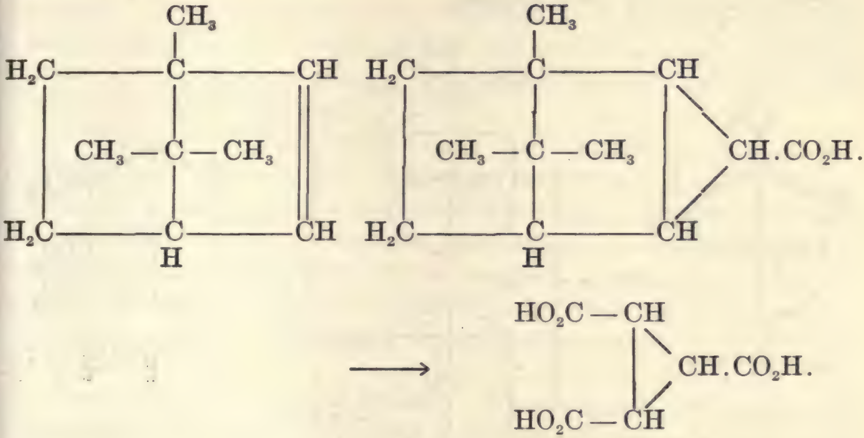
camphene

The spiro ester is stable to permanganate in suspension in sodium carbonate solution. [Buchner and Weigard also succeeded in mak-

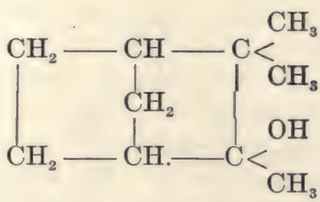
[17] Aschan, *Ann.* *410*, 240 (1915).
[18] *Ber.* *46*, 759 (1913).

ing the acid chloride, from which the amide was prepared, leaflets melting at 124°.] The purified amide readily yields the pure acid, melting at 108°. Reduction of the ester, by sodium in absolute alcohol, converts the CO_2R group to CH_2OH with rupture of the cyclopropane ring.

Applying the same method to bornylene Buchner and Weigand[19] obtained 1.2.3-cyclopropane tricarboxylic acid.



When camphene hydrochloride is carefully treated with dilute alkali, camphene hydrate is formed, which can be decomposed to camphene having the same rotatory power as the original hydrocarbon. The hydrate is therefore formed without causing any change in the carbon structure of camphene. Only two formulæ for this hydrate are possible, one being a tertiary and one a primary alcohol, but the properties of camphene hydrate are clearly those of a tertiary alcohol, i.e.,

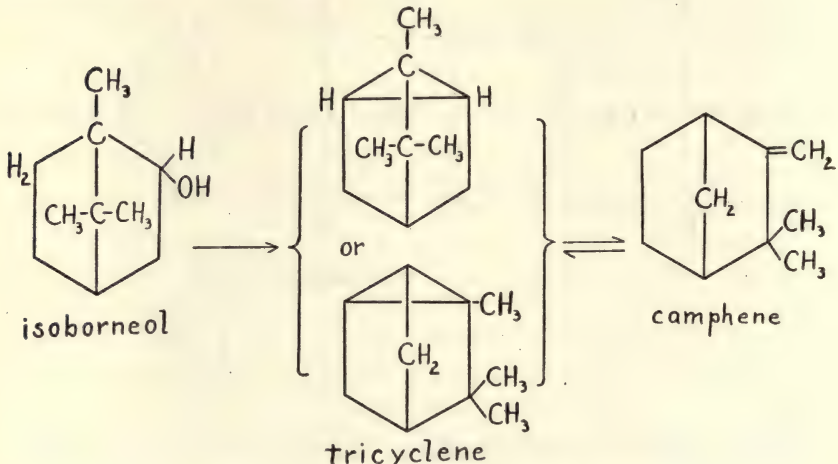


camphene hydrate

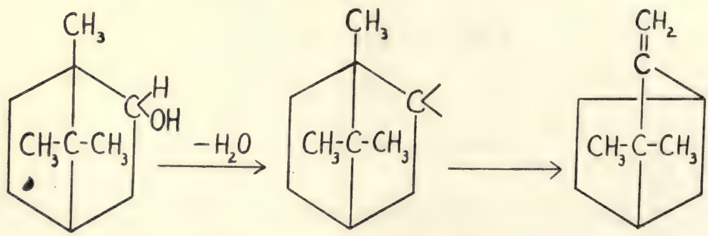
[19] *Ber.* 46, 2108 (1913). The trimethyl ester of 1.2.3-cyclopropanetricarboxylic acid melts at 56°-57°, which serves to distinguish it from its isomers.

A stereoisomeric form of camphene hydrate is methylcamphenilol, obtained by the action of magnesium-methyl iodide on camphenilone. Both forms yield camphene on dehydration and probably bear a stereochemical relation with each other comparable to borneol and isoborneol.[20]

To explain the rearrangement which occurs when isoborneol is decomposed to form camphene, the intermediate formation of tricyclene has usually been assumed,



Tiffeneau[21] has proposed the theory that when alcohols are decomposed with the formation of a hydrocarbon of a different carbon structure, as in the decomposition of pinacoline alcohol to tetramethylethylene, that the intermediate product is a hydrocarbon having a bivalent carbon atom. In the case of isoborneol and its decomposition to camphene this would be represented as follows,



[20] Aschan, *Ann.* *410*, 222 (1915).
[21] *Rev. gen. d. Sci.* *18*, 583 (1907).

Meerwein[22] has tested both of these hypotheses. Camphor hydrazone is decomposed by mercuric oxide, the intermediate compound $C_8H_{14}<\begin{matrix}CH_2\\ |\\ C=N.NH.HgOH\end{matrix}$ being decomposed with evolution of nitrogen, and it is a reasonable supposition that the bivalent carbon compound $C_8H_{14}<\begin{matrix}CH_2\\ |\\ C<\end{matrix}$ whose transitory existence is assumed by the Tiffeneau theory, would be formed and immediately rearrange to camphene, if this theory is correct. It is found, however, that tricyclene is formed almost quantitatively.

The properties of tricyclene clearly show that it cannot be an intermediate product in the conversion of isoborneol to camphene. Thus Meerwein shows that under the conditions by which isoborneol is almost quantitatively changed to camphene (heating with 33% sulfuric acid at 100°), tricyclene is practically unchanged. Also, as shown by Lipp,[23] heating tricyclene with fused zinc chloride is without effect although isoborneol is decomposed to camphene under these conditions.

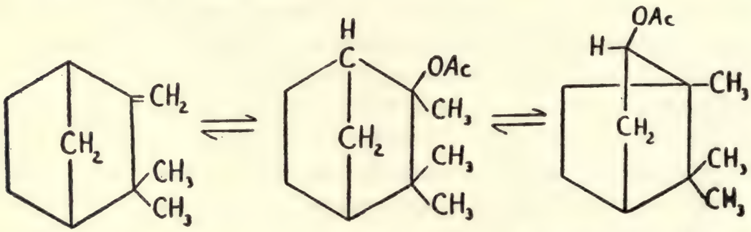
As regards the opposite reaction, the conversion of camphene to isoborneol (or acetate), Meerwein shows that chloroacetic acid reacts more rapidly with camphene than with tricyclene, and consequently tricyclene cannot be an intermediate product in the conversion of camphene to esters of isoborneol. In these experiments evidence was found that tricyclene first forms an ester of camphene hydrate. When tricyclene or camphene is treated with hydrogen chloride in cold ethereal solution, a very unstable hydrochloride is formed which Meerwein regards as the true chloride of camphene hydrate. It is so unstable that on merely shaking the chloride with water at ordinary temperatures, camphene hydrate is formed; in alcoholic caustic potash the neutralization of the alkali takes place so rapidly that the per cent of the hydrochloride present can be titrated in the cold with N/2 caustic solution during one half hour. The most striking property of this hydrochloride is its rearrangement to the chloride of isoborneol, melting-point 158°, which takes place on warming with alcoholic hydrochloric acid, which probably accounts for the fact that this camphene hydrochloride was discovered only very recently.[24]

[22] *Ber.* *53,* 1815 (1920).
[23] *Ber.* *53,* 769 (1920).
[24] Meerwein, *loc. cit.*

Thus, when hydrogen chloride is passed into a solution of camphene in alcohol the product is mainly isobornyl chloride, but also contains more or less true camphene hydrochloride, thus accounting for the various melting-points recorded in the literature for camphene hydrochloride, i.e., 118° to 158°. This chloride melting at 158° is the *iso*-bornyl chloride, evidence for which is its reduction by sodium and alcohol to camphane (dihydrobornylene) and its conversion to isobornyl acetate by treating with silver acetate in glacial acetic acid.

Isobornyl chloride is much more stable than camphene hydrochloride and is practically not affected by alcoholic caustic alkali at ordinary temperatures. Nevertheless *iso*bornyl chloride is considerably less stable than bornyl chloride (made from pinene and HCl) since by heating for one hour with alcoholic caustic alkali bornyl chloride is scarcely attacked [25] but isobornyl chloride is completely decomposed. In such a chloride mixture it is therefore possible to estimate fairly accurately the per cent of camphene hydrochloride, isobornyl and bornyl chlorides, by making use of their relative stabilities to caustic alkali.

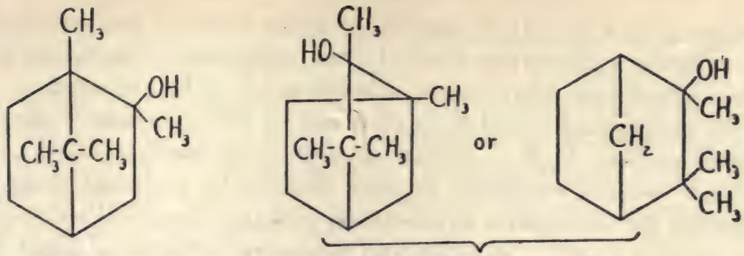
The facts point to reversible reactions between camphene and esters of camphene hydrate (chloride or acetate), and between the latter and esters of isoborneol.



camphene *acetate of camphene hydrate* *isobornyl acetate*

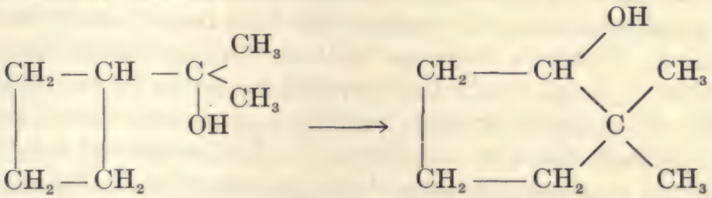
Thus, camphene hydrate can be prepared from isobornyl chloride. Methyl borneol and methyl fenchyl alcohol also appear to be in equilibrium in the presence of acids since Ruzicka [26] finds that by the action of sodium acid sulfate on either of these alcohols, the same mixture of methylcamphene and methyl-α-fenchene is obtained.

[25] Hesse, *Ber.* *39*, 1127 (1906).
[26] *Helv. chim. Acta.* *1*, 110 (1918).

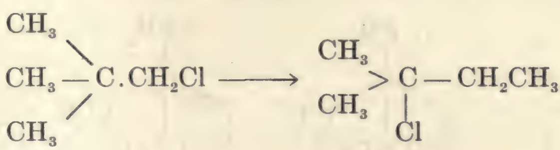


methylborneol *methylfenchyl alcohol*

Although Meerwein has produced good evidence to show that in the isoborneol ⇆ camphene rearrangement the intermediate formation of tricyclene or a hydrocarbon containing bivalent carbon is extremely improbable, the mechanism of the rearrangement is as obscure as ever. This rearrangement is to be classed with others such as that discovered by Kishner.[27]



and the well-known retropinacoline rearrangements; for example, the chloride



and the like.

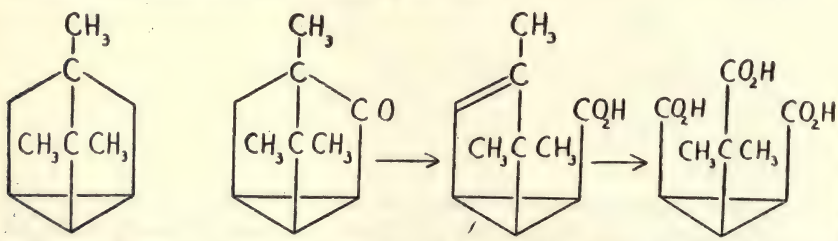
By the hydrogenation of camphene and bornylene the corresponding saturated hydrocarbons are obtained, the nomenclature of which is unfortunate. By reducing bornylene by the method of Sabatier and Senderens a "camphane" melting at 150° and boiling at 161°–162° was obtained by Henderson and Pollock [28] and the same hydrocarbon in a somewhat purer form was obtained from camphor by the decomposition of the hydrazone,[29] according to the method of Kishner, the hydrocarbon made in this way having a melting-point of 156°–157° and boiling at 161° (757 mm.). From its relation to camphor it is

[27] *Chem. Zentr.* *1908* (2), 1342; *1911* (1), 543.
[28] *J. Chem. Soc.* *97*, 1620 (1910).
[29] Wolff, *Ann.* *394*, 86 (1912).

perhaps proper to call it *camphane*, which however confuses it with the isomeric hydrocarbon derived from camphene. The terms dihydrocamphene and dihydrobornylene are much to be preferred.

By heating isoborneol with zinc dust at 220° Semmler[30] obtained a hydrocarbon, $C_{10}H_{18}$, boiling at 162° and melting at 85°, and Vavon[31] reduced camphene in ether solution by platinum black and hydrogen and obtained a hydrocarbon probably identical with Semmler's melting at 87°. Sabatier and Senderens obtained a liquid mixture from camphene which Henderson and Pollock[32] showed was a mixture of the camphane of Vavon and unsaturated hydrocarbons. The crude product obtained by Henderson and Pollock melted at 64° and the product obtained by Ipatiev,[33] "isocamphane," obtained by passing isoborneol over a mixture of nickel oxide and alumina at 215°–220° with hydrogen at 110 atmospheres, and described as melting at 63°–64.5°, is probably the crude camphane.

A product called *cyclocamphane* has been made from cyclocamphanone by Kishner's hydrazine method. Cyclocamphane melts at 117°–118°.[34] Angeli,[35] who first prepared the ketone by the action of nitrous acid on aminocamphor, regarded it as an unsaturated ketone and accordingly called it "camphenone." The presence of the three-carbon ring in camphanone was shown by converting it (through the oxime and nitrile and oxidation) to cyclocampholenic acid and by further oxidation to cycloisocamphoronic acid.



cyclocamphane *cyclocamphanone* *cyclocampholenic acid* *cycloisocamphoronic acid*, M.-P. 228°

Reduction of the ketone yields a new borneol, cyclocamphanol, melting-point 174°–176°.

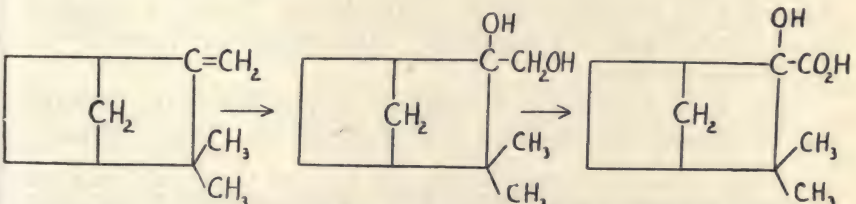
Camphene, like β-pinene, does not form a nitrosite but the nitrosite

[30] *Ber. 33,* 776 (1900).
[31] *Compt. rend. 149,* 997 (1909).
[32] *J. Chem. Soc. 107,* 1620 (1910).
[33] *Ber. 45,* 3205 (1912).
[34] Holz, *Z. angew, Chem. 27* (1), 347 (1914).
[35] *Gazz. chim. Ital. 24* (2), 44, 317 (1894).

conceivably formed as a labil intermediate product, decomposes to give nitrocamphene[36] (melting-point of *d* and *l* forms 84°–85°, *d.l.*-nitrocamphene melting at 64°–66°). Bromine also shows a similar behavior, the group $>C=CH_2$ adding Br_2 to form the labil $>CBr-CH_2Br$ which immediately decomposes to give the monobromo derivative $>C=CHBr$, camphenylidene-6-bromomethane.[37] This bromide is capable of combining with hydrogen bromide (probably reversible) to form 2-bromo-Ω-bromo-camphene, melting at 90°–91°. The corresponding camphenylidene chloride is inert to hydrogen chloride.

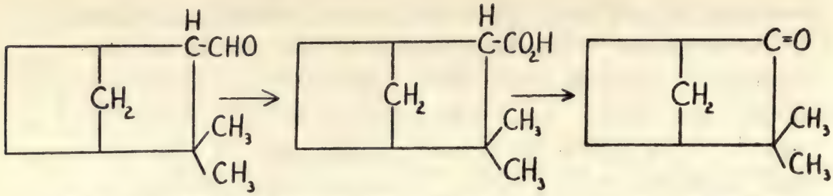
Camphene condenses with formaldehyde (trioxymethylene) in acetic acid, to form a primary alcohol, from which a large number of derivatives have been prepared. Thus, oxidation of the new alcohol yields the corresponding aldehyde, which can then react with magnesium alkyl halides to give a series of diethylenic hydrocarbons of the camphenic type.

Camphene combines with hypochlorous acid in cold dilute solutions to give a nearly quantitative yield of camphenechlorohydrin, melting at 93°. Reduction of this chlorohydrin with zinc and alcohol gives isoborneol; camphenechlorohydrin is therefore probably α-chloroisoborneol.[38] Camphenechlorohydrin reacts with caustic alkalies or moist silver oxide to form camphenilane aldehyde, which is also obtained by treating campheneglycol (obtainable by permanganate oxidation of camphene) with dilute acids. The conversion of 1.2-glycols to aldehydes or ketones by dilute acids is quite a general reaction. The principal oxidation products of camphene are shown in the following diagram,



camphene — *camphene glycol* M.-P. 200° — *α-oxycamphenilanic acid,* M.-P. 171°

[36] Lipp, *Ann.* *399*, 241 (1913).
[37] Langlois, *Ann. chim.* *12*, 265 (1920).
[38] Henderson, Heilbron & Howie, *J. Chem. Soc.* *105*, 1367 (1914).



camphenilane aldehyde M.-P. 70° *camphenilanic acid* M.-P. 65° *camphenilone* M.-P. 43°

Reduction of camphenilone by sodium and alcohol gives camphenilol, the corresponding alcohol, $C_9H_{17}OH$, melting at 84°.

Camphor.

The essential oil derived from the leaves or wood of *Cinnamomum camphora* [39] is a complex mixture from which camphor is more or less perfectly separated before the oil comes into commercial markets. According to Bertram and Wahlbaum [40] and Schimmel & Co. this essential oil contains, in addition to camphor, pinene, phellandrene, camphene, dipentene, *d.*fenchene, *d.*limonene, bisabolene, cineol, safrol, eugenol, terpineol, citronellol, borneol and cadinene. Ordinarily a light terpene fraction is separated from commercial camphor oil as this is of little value, and the heavier oil, containing large proportions of safrol and eugenol, constitutes the chief commercial source of safrol, employed for the manufacture of piperonal. In addition to the above named constituents Semmler and Rosenberg [41] isolated a bicyclic sesquiterpene boiling at 129°–133° at 8 mm.; also a monocyclic diterpene, $C_{20}H_{32}$, which they have named α-camphorene, and a second diterpene named β-camphorene which is distinguished from the α-hydrocarbon by forming a liquid hydrochloride. So-called camphorogenol reported and very imperfectly characterized by Yoshida,[42] evidently does not exist.

The physical properties of camphor, as recorded in the literature, are as follows, melting-point 175°,[43] 176.3° to 176.5°,[44] 178.4°; [45]

[39] Parry ("Chemistry of Essential Oils," Ed. 3, p. 160 [1918]), has called attention to a bulletin issued by the Monopoly Bureau, Formosa, according to which several varieties or species (?) of camphor trees are recognized but not yet distinguished botanically, whose essential oils do not yield camphor.
[40] *J. prakt. Chem.* (2) *49*, 19 (1894).
[41] *Ber. 46*, 768 (1913).
[42] *J. Chem. Soc. 47*, 782 (1885); Cf. Bertram & Wahlbaum, loc cit.
[43] Landolt, *Ann. 189*, 333 (1877); Beckmann, *Ann. 250*, 353 (1889).
[44] Foerster, *Ber. 23*, 2983 (1890).
[45] Haller, *Compt. rend. 105*, 229 (1887).

density at 18° 0.9853;[46] boiling-point 204°,[43] 209.1;[44] $[\alpha]_D$ 44.22° in 20 per cent solution in alcohol.[47] The latent heat of fusion[48] is 8.23 calories and the latent heat of vaporization is 93.4 calories.

Identification of camphor is best accomplished by preparing the oxime[49] melting-point 118° to 119°. As pointed out by Beckmann (*loc. cit.*) the oxime of *d.* camphor is lævo-rotatory and the oxime of *l.*camphor is dextro-rotatory, amounting to ± 41.3°, in alcoholic solution. The semicarbazone, melting-point 236°–238°, the p-bromophenylhydrazone[50] melting at 101°, the oxymethylene derivative melting at 80°–81° and the benzylidene compounds, have also been employed for the purpose of detecting or identifying camphor. The benzylidene compound of inactive, or synthetic, camphor melts at 78° but that of *d.* or *l.*camphor melts at 95°–96.° Camphor forms a series of compounds with mercuric iodide,[51] $C_{10}H_{14}O.Hg_2I_2$; $(C_{10}H_{14}O)_2Hg_4I_2$; $(C_{10}H_{14}O)_4Hg_5I_2$ and $(C_{10}H_{14}O)_3Hg_6I_2$. Nitric acid forms an addition product $C_{10}H_{16}O.HNO_3$, melting at 24°, and the existence of a second compound $(C_{10}H_{16}O)_2HNO_3$, melting at 2.2°, is indicated by the freezing-point curves.[52] Hydriodic acid forms $(C_{10}H_{16}O).HI$, melting at 29°–30°, and phosphoric acid forms an addition product $C_{10}H_{16}O.H_3PO_4$, melting at 29°.

Neither ordinary camphor nor its isomer epicamphor forms a cyanohydrin. Camphor, menthone, thujone and fenchone do not react with phenyl hydrazine.

The Constitution of Camphor and Its Oxidation Products.

The study of the constitution of camphor and its oxidation products and derived substances constitutes a brilliant chapter of organic chemistry, and although the structure of camphor has been known with reasonable certainty for some time, the structures of some of the derived oxidation products are still subjects of research. Since this collection of researches is such a classic and has engaged the attention of many of the ablest organic chemists, it is worth while

[46] Chautard, *Jahresber.* *1863,* 555 (for *l.*camphor); Malosse, *Compt. rend.* *154,* 1697 (1912), gives $d\frac{20°}{4°}$ 0.963.

[47] Beckmann, *loc. cit.*

[48] Jouniaux, *Bull. soc. chim.* (4) *11,* 993 (1912).

[49] Auwers, *Ber.* *22,* 605 (1889); Bredt, *Ann.* *289,* 6 (1896).

[50] Tiemann, *Ber.* *28,* 2191 (1895).

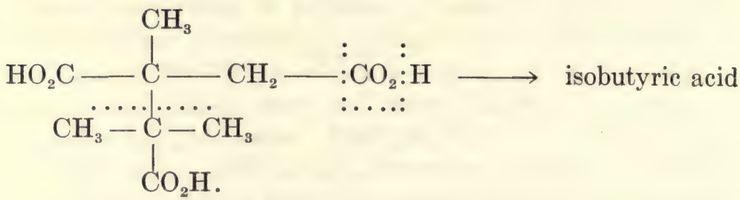
[51] Marsh and Struthers, *Proc. Chem. Soc.* *24,* 267 (1909).

[52] Shukoff & Kasatkin, *J. Russ. Phys.-Chem. Soc.* *41,* 157 (1909).

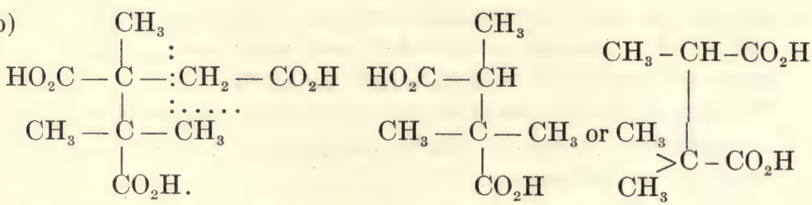
to review the matter somewhat more fully than some other related subjects. For the sake of clearness the historical method of review will not be followed.

In the earlier work undue emphasis was put upon the fact that under certain conditions camphor could be converted (with very small yields) into *para*-cymene, also to carvacrol. In 1893 Bredt[53] unraveled the structure of one of the important oxidation products of camphor, i.e., *camphoronic acid.* On heating, camphoronic acid breaks up into carbon dioxide, isobutyric acid and trimethyl succinic acid, a change which Bredt represented as follows:

(a)

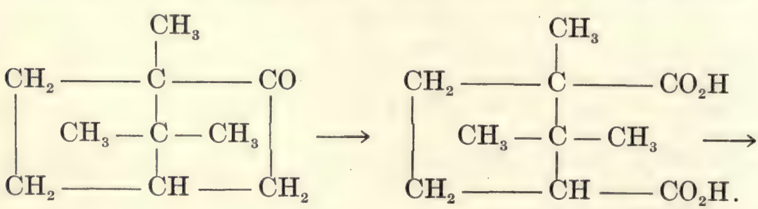


(b)



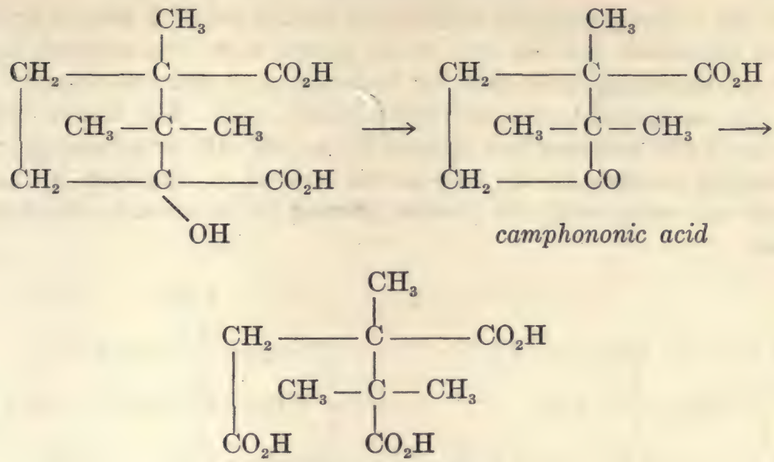
camphoronic acid *trimethylsuccinic acid*

A little later Bredt's constitution for camphoronic acid was conclusively confirmed by Perkin and Thorpe,[54] who made the acid by well-known reactions of synthesis. Bredt represented the oxidation of camphor, through camphoric acid, to camphoronic acid, as follows,



camphoric acid

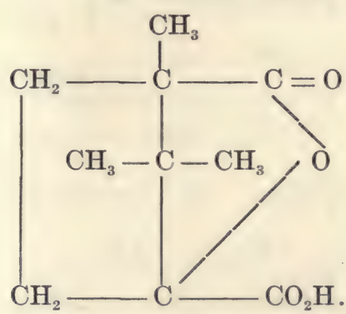
[53] *Ann.* **292**, 55 (1896); *Ber.* **26**, 3047 (1893).
[54] *J. Chem. Soc.* **71**, 1175 (1897).



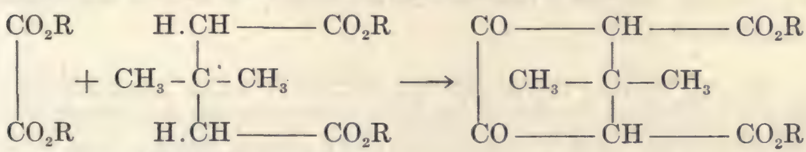
camphononic acid

camphoronic acid

The hydroxy acid shown as an intermediate product in the above series of oxidations is usually obtained in the form of the lactone, camphanic acid,

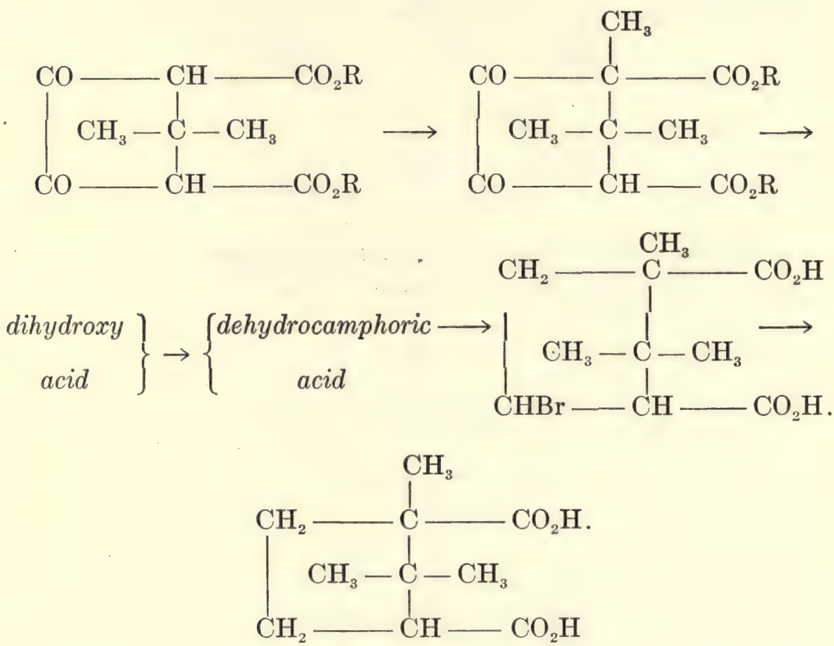


The correctness of Bredt's constitution for camphoric acid is very directly shown by the synthesis of this acid, first by Komppa [55] and later by Perkin and Thorpe.[56] By condensing ethyl oxalate with ββ-dimethylglutaric ester, by means of sodium ethoxide, Komppa obtained the diethyl ester of diketoapocamphoric acid.



[55] *Ber.* 34, 2472 (1901); 36, 4332 (1903).
[56] *J. Chem. Soc.* 89, 795 (1906).

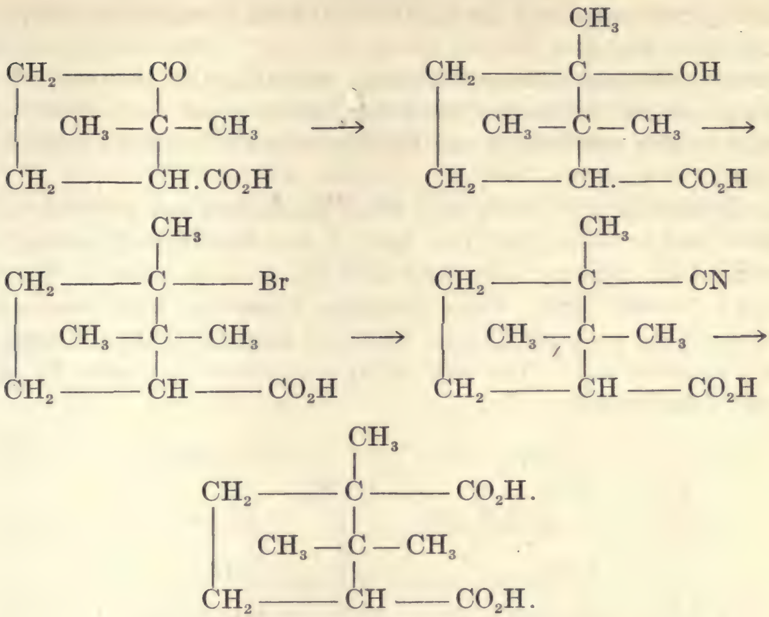
By the action of metallic sodium and methyl iodide a methyl group was introduced and the two ketone groups were then reduced, first to the dihydroxy acid, then by hydriodic acid and red phosphorus to the unsaturated acid dehydrocamphoric acid. The double bond in the latter acid was then reduced by adding HBr and reducing the resulting product by the well-known method of reduction by zinc dust and acetic acid, the product proving to be racemic camphoric acid.



r — *camphoric acid.*

Perkin and Thorpe's synthesis is even more conclusive.[57] Dimethylcyclopentanonecarboxylic ester was treated with magnesium-methyl iodide and the resulting alcohol converted first into the corresponding bromide and the latter into the nitrile, which, on hydrolysis, yields *d.l.*camphoric acid.

[57] The experimental details of Komppa's synthesis were published several years later (*Ann. 368,* 126; *370,* 209 [1909]). Blanc and J. C. Thorpe published a paper calling in question the structure of the acid obtained by methylating diketoapocamphoric ester, claiming this to be an o-methyl ether, not the c-methyl derivative (*J. Chem. Soc. 97,* 836 [1910]). After an explanatory reply by Komppa (*Ibid., 99,* 29 [1911]), Blanc and Thorpe admitted their error (*ibid., 99,* 2010 [1911]). Komppa's synthesis has not since been questioned.



The conversion of camphoric acid to camphor had already been effected by Haller.[58] Camphoric acid forms an anhydride, which on reduction by sodium amalgam, yields campholide,

$$C_8H_{14}\!\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle\!O \longrightarrow C_8H_{14}\!\left\langle\begin{matrix}CO\\ \\ CH_2\end{matrix}\right\rangle\!O$$

When campholide is heated with potassium cyanide it yields a nitrile which on hydrolysis is converted into homocamphoric acid.

$$C_8H_{14}\!\left\langle\begin{matrix}CO\\ \\ CH_2\end{matrix}\right\rangle\!O + KCN \rightarrow C_8H_{14}\!\left\langle\begin{matrix}CO_2K\\ \\ CH_2CN\end{matrix}\right. \rightarrow C_8H_{14}\!\left\langle\begin{matrix}CO_2H\\ \\ CH_2.CO_2H.\end{matrix}\right.$$

On heating the calcium salt of homocamphoric acid, Haller obtained camphor.

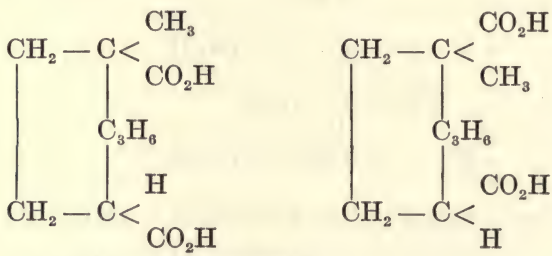
$$C_8H_{14}\!\left\langle\begin{matrix}CO_2\\ \\ CH_2CO_2\end{matrix}\right\rangle\!Ca \longrightarrow C_8H_{14}\!\left\langle\begin{matrix}CO_2\\ |\\ CH_2\end{matrix}\right.$$

Dicarboxylic acids whose carboxyl groups are separated by two or three carbon atoms readily yield anhydrides, as in the case of succinic

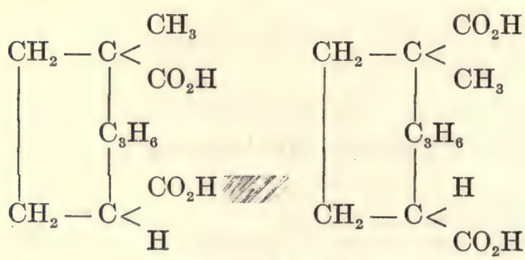
[58] *Compt. rend.* 122, 446 (1896).

and glutaric acids, and the significance of the formation of camphoric anhydride was first pointed out by Baeyer.[59] Homocamphoric acid, however, does not form an anhydride, indicating that the two carboxyl groups are separated by at least four carbon atoms, facts which agree with Bredt's constitution and the syntheses of camphoric acid, noted above.

Camphoric acid exists in a form which does not yield an anhydride and to distinguish this form it has been called *iso*camphoric acid. Like ordinary camphoric acid the *iso* acid exists in *d.* and *l.* and a racemic form. These facts also harmonize with Bredt's constitution for camphor and the chemical evidence as to the structure of camphoric acid. The four active camphoric acids may be represented as follows,



d. and l. camphoric acid



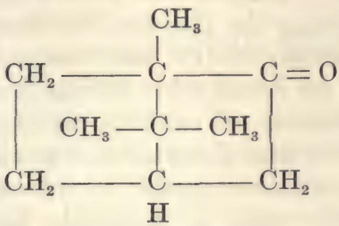
d. and l. isocamphoric acid

In camphor, however, the two carbon atoms represented by the carboxyl groups in the camphoric acids, are bound to each other and therefore there are only two active forms of camphor, i.e., *d.* and *l.*camphor, corresponding to *d.* and *l.*camphoric acid. In camphor the asymmetry is due to the CO group and optical activity disappears if

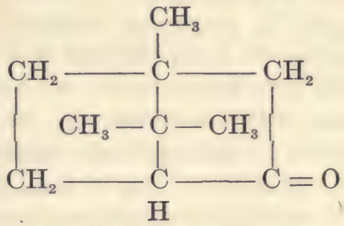
[59] *Ann.* *276*, 265. Camphoric anhydride may readily be prepared by heating the acid above its melting point, or by dehydrating by means of acetyl chloride.

this ketone group is reduced to CH_2, as was shown experimentally by Aschan.[60]

Epicamphor, or *β-camphor*. It will be evident from the structure of ordinary camphor that another isomeric ketone should be capable of existence, and, in accordance with the nomenclature suggested for the hydrocarbon camphane, ordinary camphor would be α-camphor and its isomer β-camphor. The two ketones are related structurally to each other as follows,



ordinary, or α-camphor



Epicamphor, or β-camphor

In the conversion of camphor to epicamphor a reversal of the sign of optical rotation is observed, which may be summarized thus,

$$d\text{-camphor, } [\alpha] + 39.1° \leftrightarrows l\text{-epicamphor, } [\alpha]_D - 58.2°.$$

Hydroxymethylene epicamphor, $C_8H_{14}<\begin{matrix} CO \\ | \\ C = CHOH \end{matrix}$, like ordinary hydroxymethylene camphor, is formed when *l*.epicamphor is treated with isoamyl formate and sodium in the presence of ether.[61] It exhibits muta-rotation, increasing on standing, particularly in the presence of sodium ethylate; freshly prepared material showed $[\alpha]_D$ — 125.5° and after adding a trace of sodium ethylate the rotation increased to $[\alpha]_D$ — 146.7°. The decomposition of *l*.epicamphoroxime by dilute sulfuric acid proceeds in a similar manner to that of camphoroxime, forming epicampholenonitrile, with rupture of the ring as in ordinary camphoroxime. The nitrile may be hydrolyzed to l.α-epicampholenic acid, but the behavior of this acid differs from ordinary α-campholenic acid in not rearranging to an isomeric acid corresponding to β-campholenic acid. An interesting attempt to pre-

[60] *Ann. 316*, 229 (1901).
[61] Perkin & Titley, *J. Chem. Soc. 119*, 1090 (1921).

pare β-camphor was made by Haller and Blanc.[62] Campholide, made by reduction of camphoric anhydride, yields homocamphoric acid and camphor as follows,

$$C_8H_{14}<\begin{array}{l}CO\\ \\ CH_2\end{array}>O \rightarrow C_8H_{14}<\begin{array}{l}CO_2K\\ \\ CH_2CN\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO_2H\\ \\ CH_2CO_2H\end{array} \rightarrow C_8H_{14}<\begin{array}{l}CO\\ | \\ CH_2\end{array}$$

Haller and Blanc prepared β-campholide but this substance did not react with potassium cyanide. Wagner[63] believed that he had succeeded in preparing β-borneol by applying the Bertram-Wahlbaum reaction to bornylene, but it was later shown that his bornylene must have been very impure and his results are considerably variant from those of Perkin and Bredt. Wagner's method was carefully tested by Bredt and Hilbing,[64] who employed a very pure bornylene and a mixture of borneols was obtained which they were unable to separate and on oxidation, ordinary camphor only could be identified. Epicamphor was first described in a preliminary paper by Perkin and Lankshear[65] and almost simultaneously by Bredt.[66] However much the best method of preparation was worked out by Perkin and Bredt jointly, their method consisting in treating methyl d-bornylene-3-carboxylate[67] with hydroxylamine in the presence of sodium methoxide. On heating, the product decomposes forming epicamphor, the reactions involved probably being as follows,

$$\underset{\textit{bornylene-3-hydroxamic acid}}{C_8H_{14}<\begin{array}{l}C.C(OH)=N.OH\\ \| \\ CH\end{array}} \longrightarrow C_8H_{14}<\begin{array}{l}C-N{:}C=O\\ \| \\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C.NH.CO_2H\\ \| \\ CH\end{array} \longrightarrow$$

$$C_8H_{14}<\begin{array}{l}C-NH_2\\ \| \\ CH\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}C=NH\\ | \\ CH_2\end{array} \longrightarrow \underset{\textit{epicamphor}}{C_8H_{14}<\begin{array}{l}C=O\\ | \\ CH_2\end{array}}$$

Epicamphor has an odor similar to that of ordinary camphor, it melts at 182°, boils at 213°; its oxime melts at 103°–104° and the

[62] *Compt. rend.* *141,* 697 (1905).
[63] *Ber.* *36,* 4602 (1903).
[64] *J. prakt. Chem.* (2) *84,* 783 (1911).
[65] *Proc. Chem. Soc.* *27,* 167 (1911).
[66] *Chem. Ztg.* *35,* 765 (1911).
[67] Bredt, *Ann.* *348,* 200 (1906); *366,* 1 (1909); Bredt & Perkin, *J. Chem. Soc.* *103,* 2182 (1913); Furness & Perkin, *J. Chem. Soc.* *105,* 2025 (1914).

semicarbazone melts at 237°–238°. Sodium and alcohol reduce epicamphor to the corresponding epiborneol, melting-point 181°–182.5°. Like ordinary camphor, the new ketone does not react with hydrogen cyanide and is not reduced by zinc dust in acetic acid. The chemical properties of epicamphor do not differ markedly from ordinary camphor but "favorable action of epicamphor on the beat of the heart does not become apparent until the solution administered is about four times stronger than that which produces the same effect in the case of camphor."

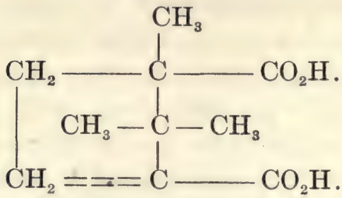
In connection with the discussion of the constitution of camphor and camphoric acid it will be convenient to review briefly several related derivatives. The nomenclature in this series of acids has been very much confused and the molecular rearrangements which some of them undergo made the determination of their constitution a matter of considerable difficulty. An extension of our knowledge of the pinacone-pinacoline rearrangement has assisted materially in clearing up the relationships of this group of substances.

Bredt[68] has reviewed the nomenclature of the camphonene and laurolene series and suggests abolishing the designations "lauronolic acid" and "campholactone." Two series of unibasic unsaturated acids are known which are derived from camphoric acid. To one series belong camphonenic acid and lauronolic acid and since the latter acid is unsaturated it may more appropriately be called laurolenic acid. Both of these acids contain a carbonyl group which is attached to the tertiary carbon atom of camphoric acid. In the other series the carbonyl group is attached to the secondary position and includes campholytic and isocampholytic acids (β-campholytic acid). It is now known that the substances formerly known as lauronolic and *iso*-lauronolic acids, bihydrolaurolactone and *iso*bihydrolaurolactone are not merely differentiated by the different positions of the double bond, as was formerly considered to be the case, but possess different carbon structures since camphonenic acid (below) (iso or γ-lauronolic acid) still contains the *gem.*dimethyl group of camphoric acid; laurolenic acid (formerly lauronolic acid) does not possess this group.

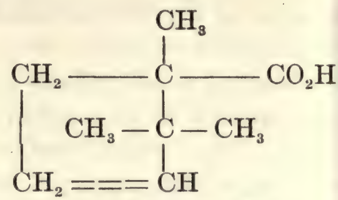
For the purpose of a key for reference, the revised nomenclature suggested by Bredt is given, as follows.

[68] *J. prakt. Chem.* (2) 87, 1 (1913).

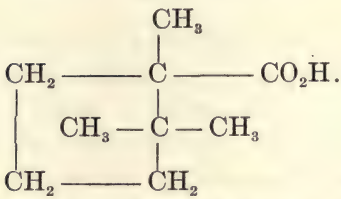
I. *Camphonene and Camphonone Series.*



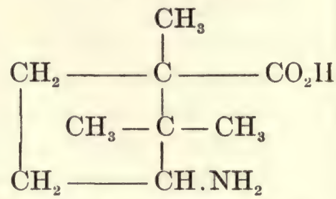
dehydrocamphoric acid



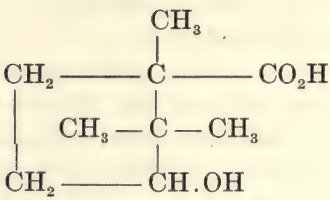
camphonenic acid.



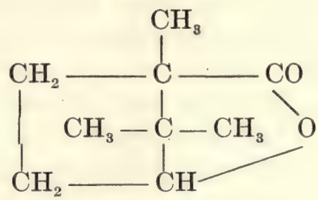
camphonanic acid.



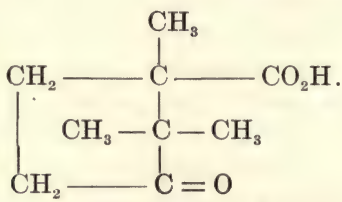
aminocamphonanic acid



camphonolic acid

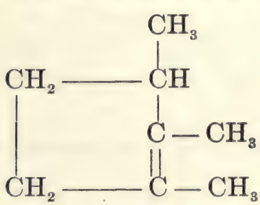


camphonololactone

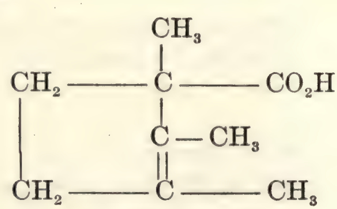


camphononic acid.

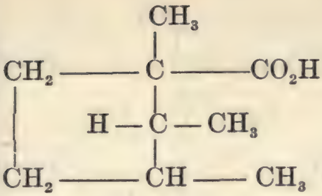
II. *Laurolene and Laurolane Series.*



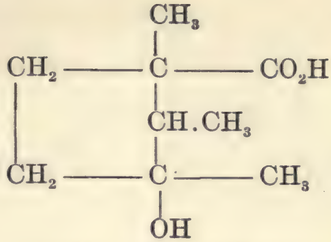
laurolene



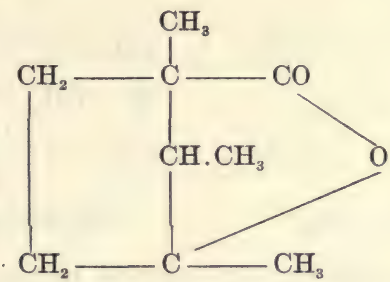
laurolenic acid



laurolanic acid



laurololic acid



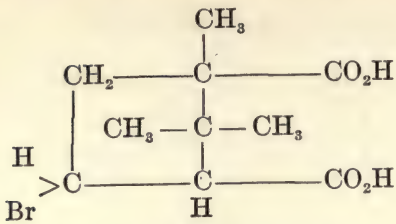
laurololactone

Some of the synonyms of the above terms are as follows:

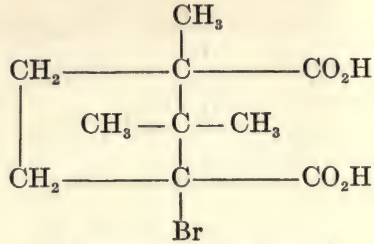
Bredt's nomenclature	*Synonym*
Camphonolic acid	Hydroxylauronic acid
Laurololic acid	Hydroxy acid of campholactone[69]
Camphonololactone	Isocampholactone[70]
Laurolanic acid	Dihydrolauronolic acid
Laurololactone	Campholactone
	Bihydrolaurolactone
Laurolenic acid	Lauronolic acid
Camphonenic acid	γ-lauronolic acid

Bredt[71] has also suggested that substituents in the single methyl group of camphoric acid be designated as Ω. Bredt follows Kipping's proposal that substituents in the *gem.*dimethyl group be designated by the letter π. Thus the four known monobromocamphoric acids are,

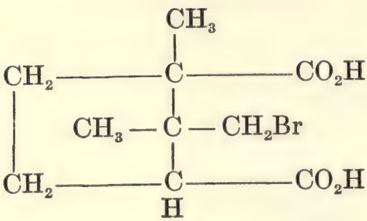
[69] Noyes, *J. Am. Chem. Soc. 34,* 182 (1912).
[70] Noyes, *J. Am. Chem. Soc. 31,* 278 (1909).
[71] *Ann. 395,* 26 (1913).



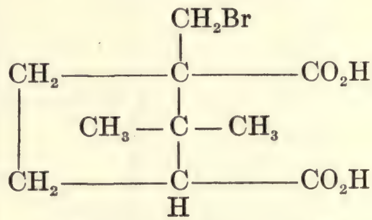
3-Bromocamphoric acid



4-Bromocamphoric acid

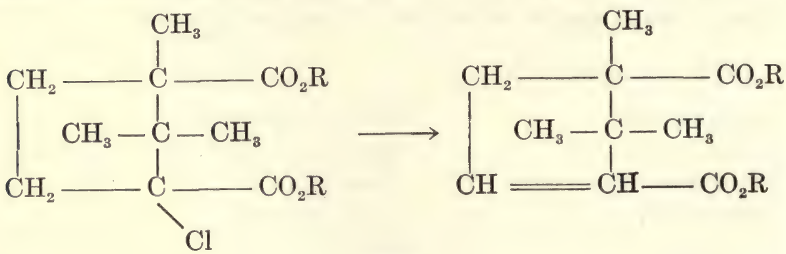


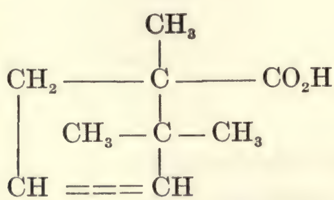
π-Bromocamphoric acid [72]



Ω-Bromocamphoric acid [73]

From chlorocamphoric phenyl ester by heating with quinoline, saponifying the resulting unsaturated ester and heating the free acid, Bredt [74] obtained an acid whose structure he represented as follows,





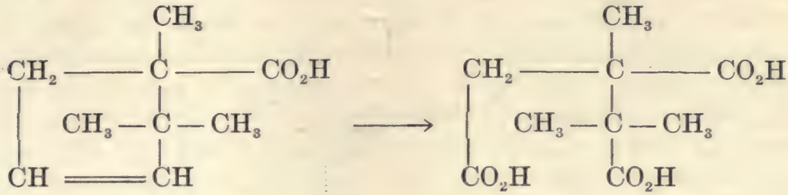
camphonenic acid

[72] Kipping, *J. Chem. Soc.* 69, 918 (1896).

[73] Armstrong & Lowry, *J. Chem. Soc.* 81, 1467 (1902).

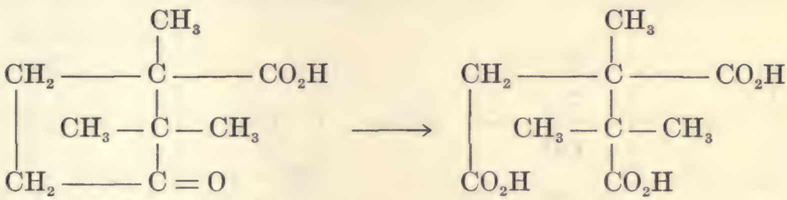
[74] *Ber.* 35, 1286 (1902). This acid was originally termed "lauronolic acid" by Bredt, but later changed to camphonenic acid to avoid confusion with Fittig and Woringer's lauronolic acid. Cf. W. A. Noyes & Burke, *J. Am. Chem. Soc.* 34, 177 (1912). In a later paper by Bredt [*Ann.* 395, 26 (1913)] *d*.dehydrocamphoric acid, melting-point 202°-203°, and *d.l*.dehydrocamphoric acid, melting-point 228°, is described.

Bredt arrived at this structure from the fact that the acid gives camphoronic acid on oxidation.



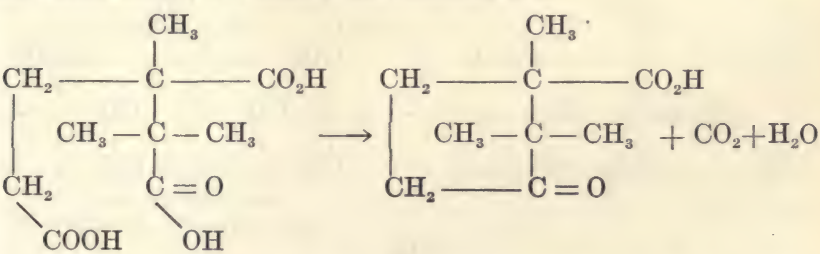
Camphoronic acid

Camphononic acid is one of the important members of this series. On further oxidation it yields camphoronic acid [75] and its constitution is as shown in the following,



camphononic acid

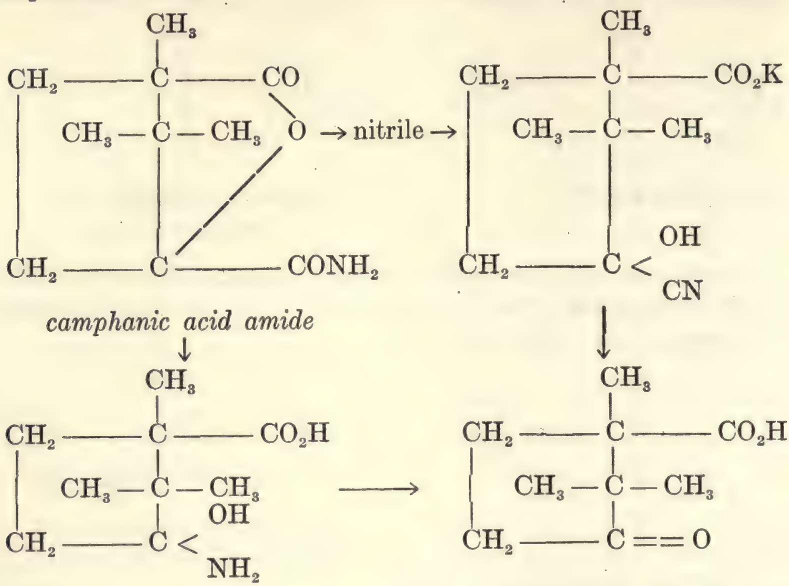
By oxidizing dibromocamphor by dilute nitric acid and silver nitrate Lapworth and Chapman [75] obtained homocamphoronic acid, whose anhydride loses CO_2 yielding camphononic acid.



Lapworth and Lenton [76] also made camphononic acid in two other ways which also indicate the constitution shown. The amide of camphanic acid was converted by dehydration to the nitrile and this, on treating with concentrated alkali loses HCN to give camphononic acid. Their second method also starts with camphanic acid amide; by treating with bromine and caustic soda the $CONH_2$ group is replaced by

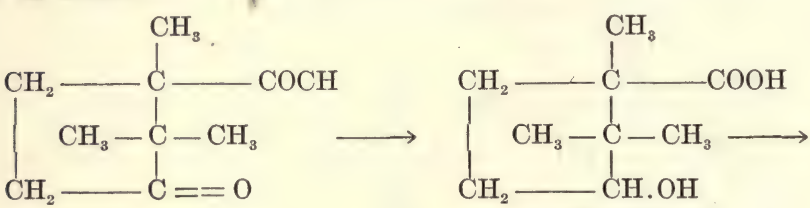
[75] Lapworth and Chapman, *J. Chem. Soc.* 75, 986 (1899).
[76] *J. Chem. Soc.* 79, 1284 (1901).

NH_2 and the resulting product decomposes yielding ammonia and camphononic acid.

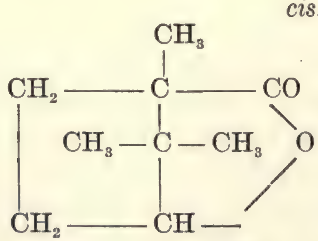


camphanic acid amide

When camphononic acid is reduced electrolytically the ketone group is reduced without structural change, to give *camphonolic acid* or its lactone.[77]



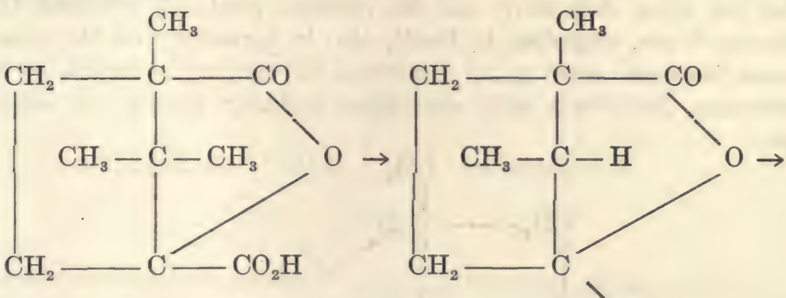
camphonolic acid
cis. trans. M.-P. 249°



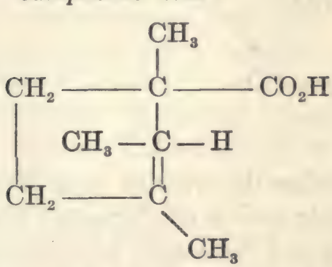
lactone M.-P. 160°

[77] Bredt, *J. prakt. Chem.* (2) *84*, 786 (1911); *Ann. 366*, 1 (1909).

It will have been noted that the above substances retain the carbon structure of camphoric acid. Fittig and Woringer[78] had obtained an acid by the decomposition of bromocamphoric anhydride which they had termed lauronolic acid but since it did not give the oxidation products described above many chemists refused to accept Bredt's proposed constitution of camphoric acid. Fittig and Woringer's lauronolic acid does not give camphoronic acid on oxidation. What appears to be the correct explanation of the structure of this acid was given by Lapworth and Lenton[79] and also confirmed by other evidence. In the preparation of Fittig and Woringer's lauronolic acid by the decomposition of camphanic acid, Lapworth and Lenton assume a *structural rearrangement* similar to the change of position of a methyl group in the pinacone—pinacoline rearrangement. Accordingly, Fittig and Woringer's lauronolic acid has the structure shown in the following.



camphanic acid

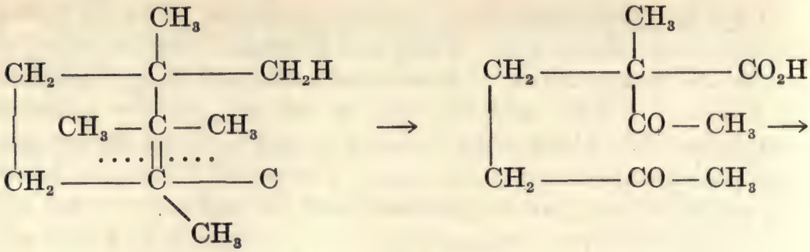


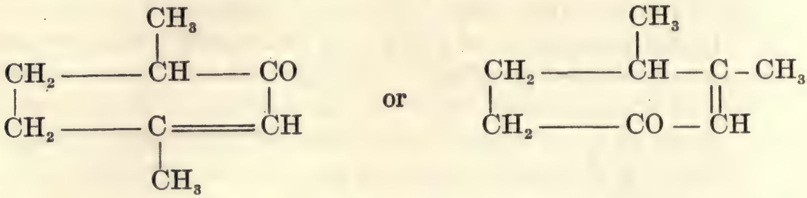
Laurolenic acid (Bredt).

(lauronolic acid)

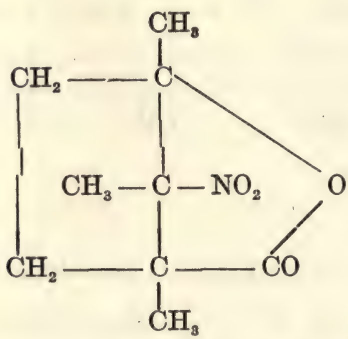
This lactone proves, in fact, to be *different* from the lactone of camphonolic acid later made by Bredt. In the light of the foregoing, other facts become clear, for example the oxidation of lauronolic acid by potassium permanganate[80] to laurenone.

[78] *Ann.* 227, 6 (1885).
[79] *Loc. cit.*
[80] Tiemann & Tigges, *Ber.* 33, 2950 (1900).





Also the nitro derivative and its reaction products, obtained by Schryver[81] are, according to Bredt, also in harmony with the other known facts, the nitro group displacing the tertiary hydrogen, as is customary, Schryver's nitro derivative probably having the structure,

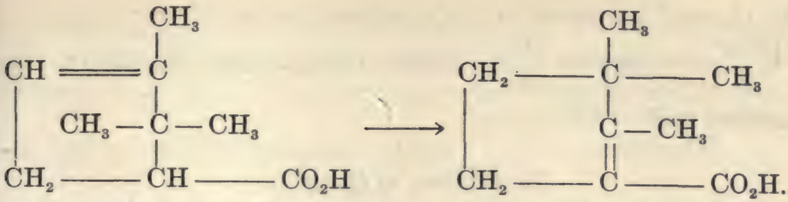


Oxidation to camphoronic acid is therefore the criterion as to whether or not the $C(CH_3)_2$ group of camphoric acid is retained, and as surmised by Lapworth and Lenton, Fittig and Woringer's lauronolic acid and its derived lactone (bihydrolaurolactone) and the hydrocarbon laurolene, do not possess this structure.

A similar rearrangement of a methyl group occurs in the conversion of campholytic acid to isocampholytic acid.[82]

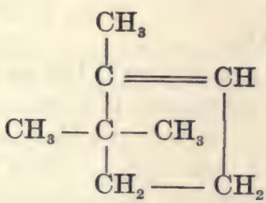
[81] *J. Chem. Soc.* 73, 559 (1898).

[82] This name has been agreed to by Noyes, Perkin, Aschan and Bredt to replace the various other names by which it has been known, e. g., isolaurolonic, camphothetic, and β-campholytic acid.



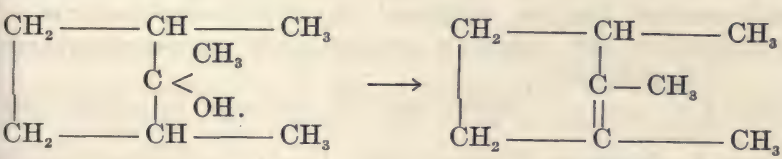
campholytic acid. *isocampholytic acid.*

In connection with the relationships just discussed it will be convenient to mention the work indicating the structure of *laurolene* and *isolaurolene* C_8H_{14}. Isolaurolene has been obtained by heating copper camphorate and also from isocampholytic acid (β-campholytic acid). Its structure has been determined by Blanc [83] by a study of its oxidation products and confirmed by its synthesis, to be 1.1.2-trimethyl-Δ^2-cyclopentene.



isolaurolene

Noyes and Derick [84] prepared laurolene by treating aminolauronic hydrochloride with sodium nitrite, also by boiling the nitroso derivative of aminolauronic anhydride with caustic soda. They found experimental evidence which they considered as supporting the structure which Eijkmann [85] had proposed on the ground of refractometric considerations. Noyes and Kyriakides [86] made the hydrocarbon by simple methods of synthesis which confirm the structure proposed by Eijkmann, i.e.,



laurolene

[83] *Bull. soc. chim.* (3) *19,* 703.
[84] *J. Am. Chem. Soc. 31,* 669 (1909).
[85] *Chem. Zentr. 1907,* II, 1208.
[86] *J. Am. Chem. Soc. 32,* 1064 (1910).

The physical properties of the laurolenes are as follows: *d*.laurolene, $[\alpha]\frac{26.2^\circ}{D} = +28.15^\circ$; $d\frac{15^\circ}{4^\circ} = 0.8030$; boiling-point 120.3°–121°. Isolaurolene boils at 108°.

Derivatives of Camphor.

Camphor Oxime[87] is readily made in good yields by adding the calculated quantity of concentrated caustic soda to an alcoholic solution of camphor and hydroxylamine hydrochloride and heating on a water bath for about one hour. The oxime crystallizes well from dilute alcohol, melting-point 120°. It boils at 249°–250° with very slight decomposition. Camphor oxime is reduced by hydrogen and catalytic nickel at 180°–200° to bornylamine, dibornylamine and camphylamine, the second being the principal product.[88]

Isonitrosocamphor, $C_8H_{14}<\begin{matrix} C=N.OH \\ | \\ CO \end{matrix}$ exists in two forms, melting at 114° and 153°.[89] For its preparation[90] 102 grams of camphor are dissolved in 500 cc. of dry ether and 15.2 grams of sodium as sodium wire, are added. Amyl nitrite is then added in small portions with cooling, until 78 grams have been added. After standing about three hours, add cracked ice and ice water; the sodium salt of isonitroso camphor is in the aqueous phase and unchanged camphor and borneol in the ether. Acetic acid precipitates the free isonitroso derivative, which after recrystallizing from dilute methyl alcohol, or petroleum ether, melts at 152°–154°.

Zinc and dilute acids readily reduce it to *amido camphor* $C_8H_{14}<\begin{matrix} CH.NH_2 \\ | \\ CO \end{matrix}$ boiling-point 244°, whose hydrochloride has a physiological action similar to curare, but feebler. Two molecules of amidocamphor may be condensed to dihydrocamphenepyrazine.[91] Amidocamphor and potassium cyanate yield camphorylcarbamide $C_8H_{14}<\begin{matrix} CH.NHCONH_2 \\ | \\ CO \end{matrix}$ which may be converted to camphorylisocyanate by the action of nitrous acid. Like the well-known reagent,

[87] Auwers, *Ber.* *22,* 605 (1889).
[88] Aloy & Brustier, *Bull. soc. chim.* (4) *9,* 733 (1911).
[89] *Chem. Zentr.* *1908,* I, 1270.
[90] Claisen & Manasse, *Ann.* *274,* 73 (1893).
[91] *Ann.* *313,* 25 (1900).

phenylisocyanate, the camphoryl derivative is very reactive and a large number of camphorylurethanes and other derivatives have been prepared from it.[92] When amidocamphor hydrochloride is treated with nitrous acid, azocamphor, $C_8H_{14}<\begin{array}{l}C=N_2\\ |\\ CO\end{array}$ is produced.[93]

Camphor Quinone, $C_8H_{14}<\begin{array}{l}CO\\ |\\ CO\end{array}$. When isonitrosocamphor is heated with dilute sulfuric acid, the diketone is formed, as in the hydrolytic decomposition of oximes,

$$\text{(a)}\quad C_8H_{14}<\begin{array}{l}C=N.OH\\ |\\ CO\end{array} + H_2O \rightarrow C_8H_{14}<\begin{array}{l}CO\\ |\\ CO\end{array} + H_2N.OH$$

$$\text{(b)}\quad C_8H_{14}<\begin{array}{l}C=N.OH\\ |\\ CO\end{array} + NO.OH \rightarrow C_8H_{14}<\begin{array}{l}CO\\ |\\ CO\end{array} + N_2O + H_2O$$

Nitrous acid also converts isonitrosocamphor to camphorquinone.[94] About 9 parts of camphor are dissolved in 15 parts acetic acid and 4 parts sodium nitrite (dissolved in minimum of water) are carefully added. After completion of the reaction the diketone is precipitated by diluting with cold water. The diketone is easily volatile, crystallizes well in yellow needles melting at 198°, and is markedly soluble in hot water.

The effect of the two contiguous CO groups upon the stability of the ring is noteworthy, the diketone being easily converted to camphoric acid or its derivatives under the influence of a wide variety of reagents.[95] The dioxime, $C_8H_{14}<\begin{array}{l}C=N.OH\\ |\\ C=N.OH\end{array}$ is best made by the action of hydroxylamine on isonitroso-camphor. All of the eight possible oximino derivatives of camphorquinone are known. The discovery of the two modifications of isonitroso*epi*camphor, constituting the third and fourth monoximes of camphor quinone, completes the list of theoretically possible oximes and Forster [96] has shown the probable configuration of these derivatives. Their physical properties are as follows,

[92] *Chem. Zentr. 1908*, I, 257.
[93] Angeli, *Ber. 26*, 1718 (1893).
[94] Claisen & Manasse, *Ann. 274*, 83 (1893) ; Lapworth, *J. Chem. Soc. 69*, 322 (1896) ; Bredt, Rochussen & Monheim, *Ann. 314*, 388 (1900).
[95] Aschan, *Ber. 30*, 657, 659 (1897).
[96] *J. Chem. Soc. 103*, 662 (1913).

	Melting-Point	$[\alpha]_D$ in Chloroform	$[\alpha]_D$ in 2% NaOH
Isonitrosocamphor (unstable)	114°	172.9°	275.3°
Isonitrosocamphor (stable)	152°	197.0°	288.0°
Isonitrosoepicamphor (unstable)	137°	–179.4°	–278.5°
Isonitrosoepicamphor (stable)	170°	–200.1°	–422.0°
Camphorquinone, α-dioxime	201°	–51.7°	–103.8°
Camphorquinone, β-dioxime	248°	.....	–24.5°
Camphorquinone, γ-dioxime	136°	16.4°	14.3°
Camphorquinone, δ-dioxime	194°	52.8°	87.0°

Reduction of the diketone by zinc dust and acetic acid gives α-oxycamphor $C_8H_{14}<\begin{matrix}CH.OH\\ |\\ CO\end{matrix}$ melting-point 203°–205°. Sodium and alcohol causes further reduction to camphorglycol, $C_8H_{14}<\begin{matrix}CH.OH\\ |\\ CH.OH\end{matrix}$, melting at 231°. This glycol may be regarded as bornyleneglycol and is not identical with the glycol of camphene. Camphor-quinone undergoes condensation with nitromethane very readily and nitromethylenecamphor and the intermediate product, nitromethylhydroxycamphor, have been isolated.[97]

$$C_8H_{14}<\begin{matrix}CO\\ |\\ CO\end{matrix} + CH_2=NO.ONa \rightarrow C_8H_{14}<\begin{matrix}C(OH).CH_2NO_2\\ |\\ CO\end{matrix}$$

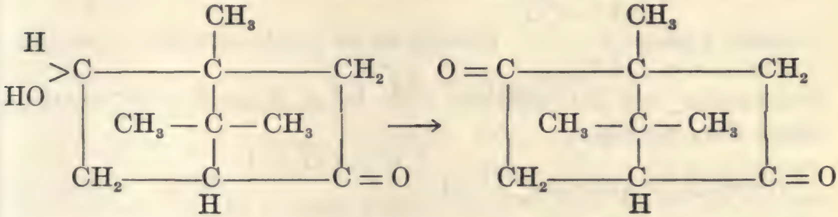
$$\longrightarrow C_8H_{14}<\begin{matrix}C=CH.NO_2\\ |\\ CO\end{matrix}$$

Condensation with ethyl cyanoacetate also readily takes place yielding ethyl camphorylidene-cyanoacetate, $C_8H_{14}<\begin{matrix}C=C<\begin{matrix}CO_2Eth\\ CN\end{matrix}\\ |\\ CO\end{matrix}$ from which the corresponding camphorylidenemalonic acid was obtained.

Para-diketocamphane: When a mixture of bornyl and isobornyl acetates are oxidized, in glacial acetic acid, by chromic acid, an *acetoxycamphor* is produced,[98] and since pure isobornyl acetate does not give this result, this derivative must be a product resulting from

[97] Forster & Withers, *J. Chem. Soc. 101*, 1328 (1912).
[98] Schrötter, *Monatsh. 1881*, 224.

the oxidation of bornyl acetate. Hydrolysis of the acetate gives hydroxycamphor, melting at 238°–246°, this product really consisting of two stereoisomerides. Oxidation of hydroxycamphor by chromic acid gives para-diketocamphane, melting-point 206.5°–207° and Bredt[99] finds that the diketone is optically active, $[\alpha]\frac{13.5°}{D} + 103.42°$. Since this substance is not identical with camphorquinone and since a substance in which both CO groups were attached to the same bridge carbon atom would be optically inactive, Bredt concludes that the constitution of the two substances are as indicated below.



Para-diketocamphane

The relative ease with which camphor reacts with metallic sodium or sodium amide to form a sodium derivative, has been made use of extensively for the preparation of other derivatives. Thus, sodium camphor in benzene solution reacts with CO_2 to give *d.camphocarbonic acid,* $C_8H_{14}<\begin{array}{l}CH.CO_2H\\|\\CO\end{array}$, melting at 128°. A recent synthesis of camphocarbonic acid by Ruzicka[100] is worth noting since a well-known reaction was successfully applied to this synthesis by the simple expedient of employing an autoclave to obtain a temperature of 200°. The diethyl ester of homocamphoric acid was condensed by sodium ethylate in alcohol at 200°.

$$C_8H_{14} < \begin{array}{l}CO_2R\\CH_2CO_2R\end{array} \rightleftharpoons C_8H_{14} < \begin{array}{l}CO\\|\\CH.CO_2R\end{array}$$

Camphocarbonic acid has been employed for the preparation of pure bornylene. The α-hydrogen atom in camphocarbonic esters is readily displaced by sodium, by which means alkylation is easily effected; alkyl halides give C-derivatives but acid chlorides give o-acylated

[99] *J. prakt. Chem.* (2) *101*, 273 (1920).
[100] *Helv. Chim. Acta. 3*, 748 (1920).

products, $C_8H_{14}<\begin{matrix} C.CO_2R \\ \| \\ C.OAc \end{matrix}$. The closely related nitrile $C_8H_{14}<\begin{matrix} CH.CN \\ | \\ CO \end{matrix}$ also forms a monosodium derivative which, by the action of alkyl iodides, yields a mixture of O and C alkyl derivatives.

Camphocarbonic acid and its alkyl derivatives readily decompose on heating, a molecule of carbon dioxide and camphor or a derivative $C_8H_{14}<\begin{matrix} CHR \\ | \\ CO \end{matrix}$ being formed. The introduction of a methyl group in this case has a very marked effect upon the melting-point, methylcamphor $C_8H_{14}<\begin{matrix} CH.CH_3 \\ | \\ CO \end{matrix}$ melting at 38°; ethylcamphor and dimethylcamphor are liquids, their odor being suggestive of menthone rather than camphor.

Oxymethylenecamphor, $C_8H_{14}<\begin{matrix} C=CH.OH \\ | \\ C=O \end{matrix}$ is of interest on account of its strongly acidic character. It is prepared by the action of methyl or ethyl formate on sodium camphor or magnesium-camphor bromide, or by the action of sodium methoxide on α-mono-halogen or α-dihalogen camphor.[101] As in similar "formyl" derivatives some reactions indicate the structure indicated above and other reactions point to the desmotropic form, $C_8H_{14}<\begin{matrix} CH.CHO \\ | \\ CO \end{matrix}$. It readily forms an acetate and a series of ethers; it combines with nascent hydrocyanic acid to give a cyanhydrine and is reduced by sodium and alcohol to *camphylglycol,* $C_8H_{14}<\begin{matrix} CH.CH_2OH \\ | \\ CHOH \end{matrix}$, which is known in two forms, *cis* melting at 87° and *trans* melting at 118°. The *trans*-glycol is oxidized by potassium permanganate to *trans*-borneolcarbonic acid $C_8H_{14}<\begin{matrix} CH.CO_2H \\ | \\ CHOH \end{matrix}$ but *cis*-borneolcarbonic acid is unstable and oxidation in this case proceeds to camphoric acid.[102]

Reduction of camphylcarbinol $C_8H_{14}<\begin{matrix} CH.CH_2OH \\ | \\ CH_2 \end{matrix}$ by sodium

[101] Brühl, *Ber.* 37, 2069 (1904).
[102] Bredt, *Ann.* 366, 62 (1909).

in moist benzene or condensation of camphylbromomethane by sodium,[103] gives dicamphylethane,

$$C_8H_{14}<\begin{matrix}CHCH_2 - CH_2CH \\ | \qquad\qquad\quad | \\ CH_2 \qquad\quad CH_2\end{matrix}>C_8H_{14},$$

melting-point 209°–211°.

Reduction of camphor by passing over catalytic nickel and alumina at 200° gives isocamphane,[104] melting-point 64.5°, boiling-point 164°–165°. Camphor condenses with oxalic ester,[105] under the influence of sodium ethylate, to camphoroxalic acid

$$C_8H_{14}<\begin{matrix}CH.COCO_2H \\ | \\ CO\end{matrix}$$

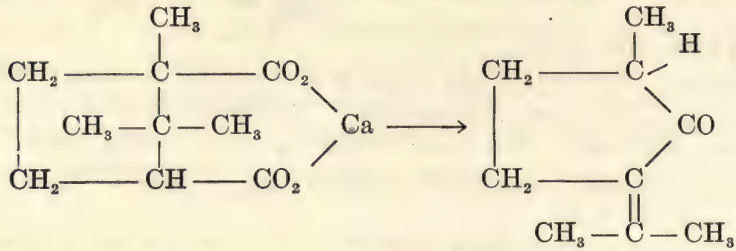
, melting-point 88°, which has yielded a series of derivatives. The above reactions will serve to make clear the very marked reactivity of the CH_2 group contiguous to the ketone group in camphor.

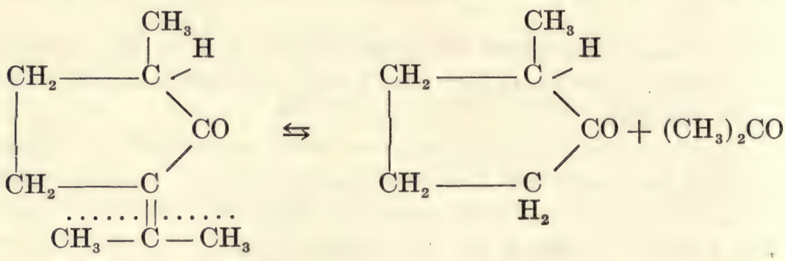
Camphoric Acid has been discussed above on account of the importance of its constitution to that of camphor itself. Its preparation is not difficult and the original method of Wreden [106] gives quite satisfactory yields. To 300 grams of camphor 3 liters of nitric acid, Sp. Gr. 1.27, are added and the mixture warmed on a water bath for several days. When cold the crude crystals are taken up in about 1 liter of water and milk of lime made from 50 grams of lime are added, which forms the freely soluble acid salt. The soluble salt is separated from unchanged camphor and the camphoric acid is then precipitated with more milk of lime as the sparingly soluble neutral salt, from which the acid may be liberated by hydrochloric acid; yield about 250 grams, melting-point 178°. It is soluble in 160 parts of water at 12° but is soluble in 10 to 12 parts of water at 100°. Inactive (*d.l.*) or para-camphoric acid melts at 204°.

On heating calcium camphorate the expected ketone formation takes place but the bridged ring is also broken, the constitution of the resulting product, camphorphorone, having been shown by a study of its oxidation products and its synthesis from 2-methyl cyclopentanone and acetone (by condensing by sodium ethoxide) and the hydrolytic decomposition of camphorone by caustic alkali to this ketone and acetone.[107] The latter reaction will recall the similar

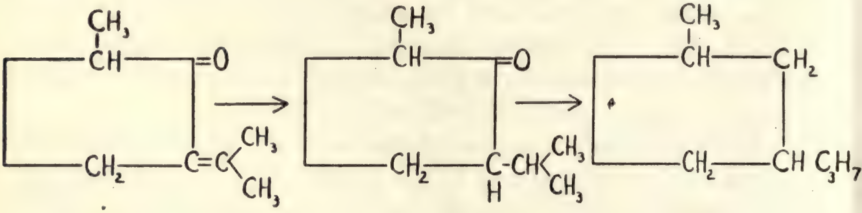
[103] Rupe & Ackermann, *Helv. Chim. Acta.* *2*, 221 (1919).
[104] Ipatiev, *Ber.* *45*, 3205 (1912).
[105] Tingle, *J. Am. Chem. Soc.* *23*, 363 (1901); *29*, 277 (1907).
[106] *Ann.* *163*, 323 (1872).
[107] Wallach, *Ann.* *331*, 322 (1904).

behavior of citral, pulegone and other substances which possess the group $(CH_3)_2C=C<$





When camphorphorone is reduced by hydrogen over catalytic nickel [108] at 130° the saturated ketone, dihydrocamphorphorone, is produced, which on reduction at a higher temperature, 280°, is further reduced to 1-methyl-3-isopropylcyclopentane (boiling-point 132°–134°).



Camphorimide, melting-point 243°, is readily made when dry ammonia is passed into boiling camphoric acid.[109]

Camphor reacts normally with magnesium-allyl bromide [110] to give allyl borneol, $C_8H_{14}<\begin{array}{l}C(OH).CH_2CH=CH_2\\ |\\ CH_2\end{array}$, which on oxida-

[108] Godchot & Taboury, *Bull. soc. chim.* (4) **13**, 599 (1913).
[109] Evans, *J. Chem. Soc.* **97**, 2237 (1910).
[110] Khoin, *J. Russ. Phys.-Chem. Soc.* **44**, 1844 (1912).

tion by permanganate yields the acid $C_8H_{14}<\begin{array}{l}C(OH).CH_2CO_2H.\\ |\\ CH_2\end{array}$

Haller has shown that by the action of alkyl halides and sodium amide, camphor may be alkylated, the substitution in such ketones replacing one or more hydrogen atoms adjacent to the carbonyl group. Haller [111] has thus prepared dimethyl, methylethyl, propyl, dipropyl, benzyl, dibenzyl and ethylbenzyl camphors. By reduction of these ketones the diethyl, methylethyl, propyl and dibenzylborneols were obtained.

The *quantitative determination of camphor* in commercial products such as celluloid or spirits of camphor is somewhat difficult on account of its volatile character. It can be precipitated from alcoholic solutions by concentrated aqueous calcium chloride,[112] taken up in light petroleum ether and finally determined gravimetrically. In the case of celluloid, distillation of the finely rasped product with steam gives fairly satisfactory results,[113] if no camphor substitutes are present. Extraction of rasped celluloid for 10 hours with petroleum ether also gives good results. The use of an immersion refractometer on solutions of camphor in methyl alcohol has also been employed.[114]

Homocamphor: This ketone closely resembles ordinary camphor in its physical properties and chemical reactions. It is a white crystalline substance melting at 189°–190°, sublimes easily and has an odor closely resembling ordinary camphor. It has one more CH_2 group, in the ring containing the CO group, than ordinary camphor. It has recently been made [115] from camphoric acid anhydride by condensing with diethyl sodio-malonate, reducing the product thus obtained and on distilling the resulting acid hydrocamphorylmalonic acid is obtained,

$$C_8H_{14}<\begin{array}{c}CO\\ \\ CO\end{array}>O \longrightarrow C_8H_{14}<\begin{array}{c}C=C(CO_2C_2H_5)_2\\ \\ CO\end{array}>O \longrightarrow$$

$$C_8H_{14}<\begin{array}{l}CH_2CH<\begin{array}{l}CO_2H\\ CO_2H\end{array}\\ CO_2H\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CH_2.CH_2CO_2H\\ \\ CO_2H\end{array} \longrightarrow$$

hydrocamphorylacetic acid.

[111] Haller & Bauer, *Compt. rend.* **158,** 754 (1914); Haller & Louvrier, *Compt. rend.* **148,** 1643 (1909).
[112] Penniman & Randall, *J. Ind. & Eng. Chem.* **6,** 926.
[113] Barthelemy, *Kunstoffe,* **3,** 46 (1913).
[114] Utz, *Chem. Abs.* I, 1467 (1907); Arnost, *Z. Nahr. Genussm.* **12,** 532.
[115] Lapworth & Royle, *J. Chem. Soc.* **117,** 744 (1920).

$$\longrightarrow C_8H_{14} < \begin{matrix} CH_2CH_2 \\ / \\ CO \end{matrix}$$

Heating the lead salt of the last named acid or prolonged heating with acetic anhydride yields homocamphor.

Synthetic Camphor

The economic balance between the cost of manufacturing camphor synthetically and obtaining it from natural sources is at present comparatively even, and success in the manufacture of synthetic camphor is very largely determined by factors over which the manufacturing chemist has no control. The development of this industry was coincident with the very great rise in price of natural camphor after Japan had succeeded in practically monopolizing the production of natural camphor. The large tree *Cinnamomum camphora* is the only commercial source of natural camphor and the production of camphor, by steam distilling the chipped wood of large mature trees of sixty years or more in age, has been carried out in China and Japan for several hundred years. True camphor was known in Europe at least as early as 1583, but owing to the custom of cutting down the trees for distillation of the wood, together with the increased demands for camphor resulting from the development of the celluloid industry, large mature trees became more and more scarce in Japan and North Central China,[116] with the result that in 1903 the industry in Japan was made a Government monopoly. Camphor had been produced in Formosa, coming into the market prior to 1895 as Chinese camphor, but after this island was acquired by Japan, camphor production was vigorously pushed by the Japanese and Formosa soon became the principal producing locality. With the elucidation of the constitution of camphor and related substances, its artificial production was practically certain to be undertaken, but this was greatly stimulated by the attempted price manipulation of the Japanese monopoly. Celluloid, the manufacture of which was first developed by John W. Hyatt of Newark, N. J., is the chief industrial use of camphor, this industry consuming seventy to eighty per cent of the world's total camphor production. The recent rapid development of the moving picture industry has added to the consumption of camphor for the manufacture of films and a further consumption has been brought about

[116] Foochow was formerly the center of the Chinese camphor market. During the period of high prices in 1919 about 930,000 lb. of camphor were shipped from Foochow.

by the manufacture of transparent films and sheets for automobile curtains. Camphor was used at one time in the manufacture of smokeless powder and it is still so used to a limited extent in some sporting powders. The United States imports the largest share of the annual production of natural camphor but with the development of the celluloid industry by the Japanese, the Japanese Monopoly Board has seen fit to *allot* certain proportions of the output to the various consuming countries, a situation which is having the natural result of stimulating the production of natural camphor in the United States.

All of the successful processes for the manufacture of artificial camphor employ pinene or turpentine as a raw material, and while the primeval camphor forests in Formosa and the interior of China are being rapidly destroyed, the manufacture of artificial camphor is dependent upon a raw material the supply of which is likewise rapidly diminishing with the destruction of the American turpentine forests. Turpentine is the largest item of cost in the manufacture of artificial camphor. However, the use of light petroleum fractions and other turpentine substitutes, particularly in the paint and varnish industry, should enable scientific forestry to keep pace with the consumption of turpentine in those industries in which it is indispensable.

Another factor in the situation is the planting of camphor trees and the distillation of camphor from the twigs and leaves. (The camphor tree does not exude an oleoresin which can be collected and separately distilled, as in the case of turpentine.) The cultivation of camphor trees and distillation of the leaves has been carried out experimentally in numerous subtropical localities, the Bahamas,[117] Florida, Ceylon, Java and Formosa, and according to a recent Bulletin of the Imperial Institute (1920) the Japanese Monopoly Board are stated to have planted 3,000,000 trees between the years 1900 and 1906 and 11,000,000 trees in the three years following. In 1913 the Board adopted the plan of planting 3,000 acres annually in camphor trees. However, leaf distillation has not proven economical and the total production of Formosan camphor has declined steadily since 1916. In 1919 the Japanese Monopoly Board estimated that the production of Formosan camphor from old trees would average about 6,500,000 lb. annually and that the trees set out previously, as before mentioned, would be ready for working about 1930. In the United

[117] Emerson & Weidlein, *J. Ind. & Eng. Chem.* *4*, 33 (1912); Eaton, *U. S. Dept Agric. Bull. 15* (1912); Beille & Lemaire, *Bull. de Pharmacie Bordeaux 1913*, 521.

States one celluloid company has about 3,000 acres planted in camphor trees near Satsuma, Florida, and another company is reported to have about 12,000 acres planted in camphor near Waller, Florida. The United States Department of Agriculture has a station at Orange City, California, engaged in the study of camphor cultivation. The cultivation of camphor and distillation of the leaves has also been studied in the Federated Malay States and at the Hakgala Gardens in Ceylon. In the former tests the yield of crude camphor varied from 1.1 to 2.6 per cent; a yield of about 180 pounds per acre per year was estimated. Old wood of mature trees yields on an average about 4 per cent of crude camphor oil, and air dry leaves of cultivated trees average 1.5 to 2 per cent of camphor oil (75 per cent of which is camphor). R. T. Baker[118] has reported a high yield of camphor from the Australian species *Cinnamomum olivieri* and *C. laubatii.*

Formerly, crystalline bornyl chloride (usually miscalled pinene hydrochloride) was manufactured and sold under the name of "artificial camphor." This product has been known for more than a century but its usefulness in the manufacture of true camphor was not appreciated until the development, since 1906, of the processes now employed in the making of synthetic camphor. Bornyl chloride cannot be substituted for camphor in the manufacture of celluloid and it contains unstable hydrochlorides, which liberate free hydrochloric acid. It is no longer a common commercial article.

All known processes for the industrial manufacture of synthetic camphor involve the oxidation of borneol or isoborneol. Borneol occurs in nature as "Borneo camphor" in the wood of one of the *Dipterocarpaceæ* and in a large number of essential oils, including most of the pine needle and cedar leaf oils, ginger oil, et cetera, but from none of these natural sources can it be produced cheaply or in quantity. The borneols are obtained industrially from bornyl chloride, and this explains the use of pinene or turpentine as a raw material. No other material is known from which the borneols or camphor can be manufactured cheaply and in quantity.

Turpentines suitable for the production of bornyl chloride and synthetic camphor are derived mostly from the long leaf pine, *Pinus palustris*, of the southern United States, the Cuban pine, *Pinus heterophylla*, and the *Pinus pinaster* of France. The turpentines from these species consist almost exclusively of α and β-pinenes. Small proportions of limonene and phellandrene might occasionally be found in

[118] Schimmel & Co. Semi-Ann. Rep. *1911* (1), 38.

American turpentine since, as Herty and Dickson[119] have shown *Pinus serotina* yields a so-called turpentine consisting chiefly of limonene, but these trees are scattered and relatively unimportant. Sylvestrene, one of the principal constituents of Russian and Finnish turpentine, has never been found in the oil from American species. The various "process turpentines," made by solvent extraction of pine wood or from stumps, is not suitable for the manufacture of bornyl chloride since such turpentines commonly contain liberal proportions of the solvent employed for its extraction, and other constituents which have been noted in such oils are limonene or dipentene, cineol, terpineols, terpinene and fenchyl alcohol. Turpentine is considerably modified by air oxidation, forming alcohols, terpineols, sobrerol, formic and acetic acids and resinous substances, and since moisture must be rigidly excluded from the preparation of bornyl chloride, the presence of very small traces of alcoholic or other oxidation products, which can form water by the interaction of hydrogen chloride, very materially decreases the yield of bornyl chloride and the use of old turpentine which has been exposed to air oxidation should accordingly be avoided.

Testing of Turpentine:

(a) *Specific Gravity:* This should be within the limits 0.862 to 0.870 at 20°C. Lower specific gravity would indicate the presence of petroleum naphtha. A higher specific gravity would indicate the presence of wood turpentine, "pine oil" (terpineols), or that the turpentine has become oxidized by long storage.

(b) *Boiling-point:* Nothing should distill below 154°C. (except a drop or two of water), and 75% should distill below 160°. Some specifications require that 95% should distill below 170°. Petroleum naphthas are sometimes very closely cut so as to boil within this range (154° to 170°), but ordinarily will show some distillate below 154°. Limonene and dipentene boil at 176° and any considerable amount will be thus indicated. The terpineols boil at 210°–218°. Rosin spirit has a wide range of boiling-point, like petroleum naphtha, and also contains considerable dipentene.

(c) *Optical Rotation:* It is not known whether pinenes of low optical rotation give better yields of bornyl chloride, as is the case with crystalline nitrosyl chlorides, or not.

[119] *J. Am. Chem. Soc.* **30**, 872 (1908).

(d) *Refractive Index:* At 20°C. this should be within the limits 1.4680 to 1.4760. Low values would indicate petroleum naphtha.

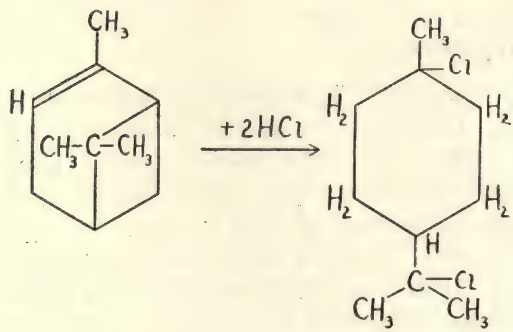
(e) *Bromine and Iodine Numbers:* These are chiefly useful in detecting petroleum naphtha but are hardly necessary when the other tests are made. It is difficult to carry out these determinations and get accurate, concordant results as with fatty oils, owing to substitution reactions taking place with formation of halogen acid.

Effect of Other Constituents on Bornyl Chloride Preparation:

(1) β-pinene yields the same hydrochloride as α-pinene:

(2) *Camphene*, a minor constituent of turpentine oil, yields a low melting, unstable hydrochloride which probably yields camphene readily in the autoclave process. Its presence is not objectionable but is partly responsible for the partial decomposition of the crude bornyl chloride, free HCl being given off.

(3) *Water:* The presence of moisture in the reaction mixture causes the pinene to be converted chiefly into dipentene dihydrochloride.



which melts, when pure, at 50°, but the impure mixture remains oily and retains considerable bornyl chloride in solution. Dipentene dihydrochloride is much less stable than bornyl chloride and when such an oily mixture is heated, it is readily decomposed to free HCl and dipentene.

(4) *Limonene*, the optically active form of dipentene, forms the dihydrochloride and diminishes the yield of bornyl chloride in the manner indicated above.

(5) *Terpineols and other Alcohols* yield water when treated with HCl; cf. item (3).

(6) *Organic acids* also cause the reaction with hydrogen chloride to go too far, with rupture of the C_5 ring to form dipentene dihydrochloride.

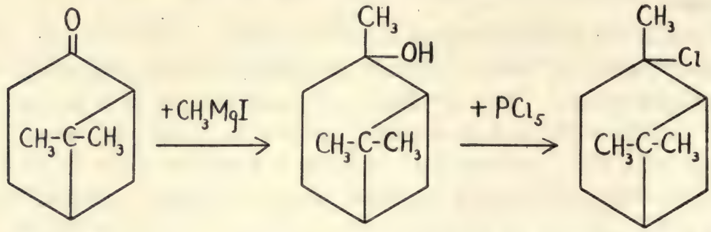
Distillation and Drying of the Turpentine: The secret of obtaining good yields of bornyl chloride is effective drying and purification of the turpentine. Mere drying is not sufficient as it is necessary to remove or destroy alcohols or other substances which yield water when treated with HCl, and metallic sodium is therefore best for this dual purpose. The still, which may be of iron or copper, should be provided with a stirrer so that after the sodium is melted it will be thoroughly emulsified in the oil. A small fractionating column is advisable, in which case 90 per cent of American turpentine can be used for the preparation of bornyl chloride.

Turpentine and Hydrogen Chloride: When the pinene has been well dried and purified from oxidation products and the hydrogen chloride is carefully dried, preferably by sulfuric acid Sp. Gr. 1.84, a yield of bornyl chloride corresponding to about 75 per cent of the theory can be obtained. Lead-lined or glass-enameled mixing vessels should be employed; iron, or alloys or other material which can yield iron chloride give liquid chlorides. Reaction temperatures above 30° yield increasing proportions of liquid chlorides but the reaction with hydrogen chloride is slow below —15°. Dry neutral solvents such as petroleum ether or carbon tetrachloride can be employed without diminishing the yield of bornyl chloride and the solidification of the reaction mixture can thus be prevented, but alcohol, ether or glacial acetic acid cause liquid chlorides to be formed.

Bornyl chloride is remarkably stable for a chlorine derivative of the non-benzenoid hydrocarbon series. The statements in the earlier literature that it is decomposed slowly at room temperature and fairly rapidly at 100° probably refers to the decomposition of the crude product containing unstable impurities such as dipentene dihydrochloride and camphene hydrochloride. Wallach [120] states that bornyl chloride distills practically without decomposition at 207°–208°, a fact which is familiar to those experienced in this field. Bornyl chloride, once formed, is not changed by further treatment with hydrogen chloride, either dry or in the presence of moisture. True pinene hydrochloride is readily converted to dipentene dihydrochloride by HCl. Pinene hydrochloride has never been isolated from the products of

[120] *Ann.* **239**, 4 (1887).

the reaction of pinene and hydrogen chloride but was made by Wallach[121] from nopinone by means of magnesium-methyl iodide.



nopinone *pinene hydrochloride*

The mixture of oily chlorides accompanying the crude bornyl chloride contains nearly 50 per cent of bornyl chloride in solution; thus, equal quantities of bornyl chloride melting at 131° and dipentene dihydrochloride melting at 50°, melt down to an oil at room temperature 20° to 22°, and fenchyl chloride, which is an oil, has a similar solvent effect. When the oily chloride mixture is heated to about 180°, the unstable chlorides are decomposed and a fairly brisk liberation of hydrogen chloride results. The resulting terpenes, chiefly dipentene, may then be distilled and the subsequent fractions boiling from 185°–215° yield an additional quantity of crystalline bornyl chloride. About 10 per cent of the original oily chloride mixture remains behind as a heavy viscous mixture of polymers. The amount of crystalline bornyl chloride which is recoverable in this way is equivalent to about 35 to 38 per cent of the original oily chlorides, when these chlorides are separated originally at — 15°.

The formation of bornyl chloride from pinene and hydrogen chloride is exothermic.[122]

On account of the extraordinary stability of bornyl chloride many attempts have been made to employ catalysts to facilitate either the formation of camphene or conversion to bornyl esters. Anhydrous aluminum chloride reacts energetically with bornyl chloride, evolving hydrogen chloride and causing further decomposition and polymerization. Anhydrous ferric chloride is markedly less active and fused zinc chloride is still less active. Stannic chloride and titanium chloride are much like zinc chloride in their effect on bornyl chloride. Cuprous chloride, or finely divided copper, is claimed to have a cata-

[121] *Ann.* *356,* 227 (1907).

[122] Guiselin, *Chem. Ztg.* *34,* 1299 (1910). Large scale work showed 119,000 calories are liberated on treating 100 kilos of turpentine.

lytic effect upon a wide variety of reactions of both alkyl and aryl chlorides, as in the manufacture of glycol,[123] or the conversion of chlorobenzene to phenol,[124] but appears to be of no value in reactions of bornyl chloride. Barium chloride markedly catalyzes the decomposition of simple alkyl chlorides to olefines[125] and calcium chloride causes rapid condensation of benzyl chloride. But zinc chloride appears to be the only catalyst appearing in the patent literature of the bornyl chloride reactions.[126] The purpose of this catalyst is to avoid the higher temperatures and pressures usually necessary for the complete conversion of bornyl chloride to camphene and bornyl acetate, when acetic acid and sodium acetate are used. However, considerable polymerization invariably takes place and one patentee[127] seeks to avoid this by introducing sodium acetate at intervals which has the effect of converting the zinc chloride into zinc acetate and sodium chloride, the latter separating on account of its slight solubility in acetic acid. Another patentee refluxes a solution of bornyl chloride in formic or acetic acids and adds zinc formate or acetate.[128] These reactions are quite analogous to the conversion of chloropentanes to amyl acetates by heating with sodium acetate in acetic acid solutions. In both cases zinc salts cause the formation of 10 to 25 per cent of heavy viscous polymerized hydrocarbons.

Conversion of Bornyl Chloride to Camphene and Bornyl Acetate.

In the following discussion no attempt is made to distinguish between camphene and bornylene.

The difficulty with most of the processes for making camphene from bornyl chloride by heating with alkalies, is chiefly a mechanical one, i. e., the insolubility of bornyl chloride in alkalies and inorganic alkaline mixtures. Naturally vigorous agitation affords better contact of the reacting substances and the presence of a fine solid suspension, milk of lime, assists in the emulsification.[129] The addition of fatty acid soaps has been proposed[130] and molten alkali phenolates[131] also have been suggested. Complete miscibility is obtained

[123] Matter, U. S. Pat. 1,237,076.
[124] Meyer & Bergius, U. S. Pat. 1,062,351; *Ber.* *47*, 3155 (1914).
[125] Braun & Deutsch, *Ber.* *45*, 1271 (1912).
[126] Bergs, U. S. Pat. 903,047; Weizman, U. S. Pat. 910,978; von Heyden, U. S. Pat. 919,762.
[127] Ruder, U. S. Pat. 1,105,378.
[128] Philipp, U. S. Pat. 919,762.
[129] Schmitz & Stalman, U. S. Pat. 1,030,334.
[130] Stephan, U. S. Pat. 725,890.
[131] Koch, U. S. Pat. 970,829; Bergs, U. S. Pat. 833,666.

when bornyl chloride is heated with organic bases such as aniline,[132] naphthylamine,[133] pyridine,[134] or alcoholic ammonia.[135] The aniline process gives very good yields, about 90 per cent of the theory but an excess of aniline is necessary, as otherwise, bornyl aniline hydrochloride is formed and this substance is not easily decomposed.

When bornyl chloride is heated with sodium acetate in acetic acid in an autoclave to 180° to 200° the bornyl chloride is almost quantitatively converted into camphene[136] and bornyl acetate. The camphene and acetic acid may be distilled together from the resulting reaction mixture and converted to bornyl acetate by the addition of a small quantity of sulfuric acid according to the well-known method of Bertram and Wahlbaum. (In order to separate the bornyl acetate thus formed from the excess acetic acid without diluting with water, a slight excess of sodium acetate may be added to form sodium sulfate and acetic acid, followed by fractional distillation *in vacuo*.)

Bertram and Wahlbaum[137] originally recommended acetylating camphene at 50°, using a mixture such as the following: 2000 cc. acetic acid, 1000 cc. camphene, 50 cc. water and 50 g. sulfuric acid. Verley[138] recommends much more water, as indicated by the following: 450 parts sulfuric acid diluted to 60 to 66 per cent, 100 parts camphene, 100 parts acetic acid, the mixture being vigorously agitated at 30°. Still better results, according to the writer's experience, are obtained by the method of Behal,[139] according to which the Bertram-Wahlbaum mixture is allowed to stand at room temperature for 24 hours. The formation of polymers is much reduced by operating at the lower temperatures. With pure camphene the yield of bornyl acetate is 92 to 94 per cent of the theory. When the resulting bornyl acetate is fractioned in vacuo, unchanged hydrocarbons pass over with the acetic acid fractions. Several other modifications of the Bertram-Wahlbaum reaction are obviously mere patent word play.

It is possible that sodium formate and formic acid can be substituted for acetic acid and acetate; in fact, such a process is described by Dubosc.[140] Henry has shown that sodium formate in methyl alcohol, and an alkyl halide, gives excellent yields of the corresponding

[132] German Pat. 205,850 (1907); Brühl, *Ber.* *25*, 146 (1892); Ullmann & Schmid, *Ber.* *43*, 3202 (1910).
[133] German Pat. 206,386 (1907).
[134] Weizmann, U. S. Pat. 896,962.
[135] German Pat. 264,246 (1912).
[136] Wallach, *Ann.* *252*, 6.
[137] *J. prakt. Chem.* (2) *49*, 1 (1894); German Pat. 67,255.
[138] U. S. Pat. 907,428 (1908).
[139] Austrian Pat. 38,203 (1908).
[140] Brit. Pat. 14,379 (1907).

alcohol,[141] and ethylene chloride can be smoothly converted to the glycol by this reaction.[142] Bornyl chloride is so remarkably stable, however, that, when using methanol, the reaction is slow at 180° and 330 lbs. pressure. Heating bornyl chloride with alkali oxalates has also been tried.[143]

Other Processes for Manufacturing Borneol or Bornyl Esters.

The first attempt to manufacture artificial camphor on an industrial scale was in 1900 at Niagara Falls, where the Thurlow process[144] was operated by the Ampere Electrochemical Co. At that time, turpentine could be had for about 35 cents per gallon but the yields of borneol were so low that the cost of artificial camphor by this method was considerably greater than the market price of natural camphor and the process was accordingly soon abandoned. In the Thurlow process anhydrous oxalic acid was added to dry turpentine at 120°–130°. The reaction is energetic and much material was lost by the reaction becoming too violent. Dipentene was separated from borneol esters by distilling with steam, the esters saponified and the borneol oxidized to camphor by chromic acid mixture. It was found most expedient to purify the borneol before oxidation rather than to purify the camphor made from impure borneol.

The Thurlow process had quite a few European modifications. Zeitschel[145] heated pinene and glacial acetic acid to 200° for five hours and reported a yield of 10 to 15 per cent camphene, about 40 per cent bornyl acetate and the remainder was dipentene. According to the writer's experience the yields of camphene and bornyl acetate are not improved by the addition of acetic anhydride. Fenchyl alcohol is also formed and Bouchardat and Lafont observed[146] the formation of fenchyl alcohol when using benzoic acid under similar conditions. Bischler and Baselli[147] treated camphene with anhydrous oxalic acid at 110°–115°; Seifert[148] used salicyclic acid and pinene at 110° for 50 hours; Austerweil[149] used "poly-substituted acids"; Hertkorn[150] heated turpentine with boric acid and absolute alcohol, etc.

[141] *Bull. acad. roy. Belg. 1902,* 445.
[142] Brooks and Humphrey, U. S. Pat. 1,215,903; *J. Ind. & Eng. Chem. 9,* 750 (1917).
[143] Charles, Eng. Pat. 5,549 (1904).
[144] U. S. Pat. 698,761; 833,095.
[145] U. S. Pat. 907,941.
[146] *Compt. rend. 113,* 551.
[147] U. S. Pat. 876,310.
[148] U. S. Pat. 779,377.
[149] U. S. Pat. 986,038.
[150] U. S. Pat. 901,293.

It is claimed [151] that by the action of tetrachlorophthalic acid on turpentine at 106°–108° (12 hours) and finally at 140° (six hours) that esters of borneol are formed and that the borneol thus obtained, after saponification of the ester, is quite free from isoborneol. This method should therefore be operated to advantage in conjunction with the method of catalytically oxidizing the borneol to camphor by passing over heated copper, since isoborneol is chiefly decomposed to camphene by this treatment.

Hesse [152] has described the reaction of bornyl chloride, with magnesium in ether, as in the well-known Grignard reaction, and oxidizing the magnesium-bornyl chloride by air or oxygen to obtain borneol. This reaction, although patented, is of little interest since, like all the more complex alkyl halides, the reaction with magnesium is very slow and the main reaction is one of condensation,

$$\text{(a)} \qquad C_{10}H_{17}Cl + Mg \longrightarrow C_{10}H_{17}MgCl$$

$$\text{(b)} \qquad C_{10}H_{17}MgCl + C_{10}H_{17}Cl \longrightarrow MgCl_2 + C_{20}H_{34}$$

Regardless of its high cost, this method is not even a good laboratory method.

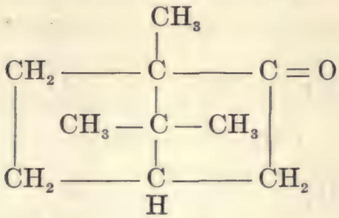
By reacting upon bornyl chloride with milk of lime vigorously stirred, at a comparatively low temperature, 135° to 150° for about three days, an alcohol isomeric with borneol is obtained.[153] This alcohol, camphene hydrate, is much less stable than borneol, melts at 149°–150°, boils at 206° and on heating with dilute acids is readily converted to camphene. This instability would indicate the structure of a tertiary alcohol but its constitution is not yet definitely known.

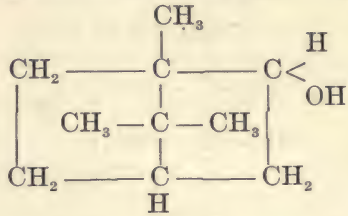
The treatment of pinene with ozone has also been described in a patented process [154] but hydrolysis of pinene ozonide does not really give borneol or camphor but pinonic acids (q.v.) and a series of other products. Bornylene ozonide might be expected to give camphor on hydrolysis. The oxidation of borneols to camphor by ozone has also been patented [155] but the industrial value of all oxidation methods depending upon ozone is questionable.

[151] Brit. Pat. 144,604, to Fabriques de produits chimiques de Than et de Mulhouse.
[152] U. S. Pat. 826,165; 826,166.
[153] Schering, German Pat. 219,243 (1908); *Ber.* *41*, 1092 (1908).
[154] Knox, U. S. Pat. 1,086,372 (1914).
[155] Stephan & Hunsalz, U. S. Pat. 801,483 (1905).

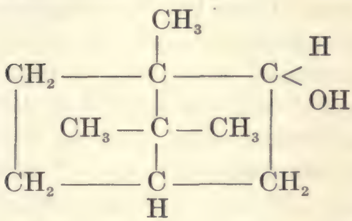
Borneol and Isoborneol

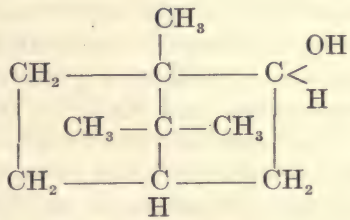
The relation of camphor to borneol is shown by the formation of borneol from camphor by reduction by sodium and alcohol.





In addition to borneol, the closely related *iso*borneol is also formed in this reaction. The two borneols are commonly believed to be stereoisomers, i. e.,



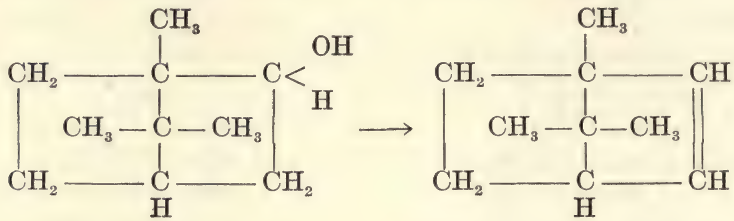


Both yield camphor on oxidation and their behaviors on oxidation are nearly identical and for the purpose of manufacturing synthetic camphor need not be separately considered. Isoborneol is the principal product of the hydration of camphene in the Bertram-Walbaum reaction. Isoborneol is somewhat less stable than borneol and yields a "camphene," melting-point 50°, when decomposed by the action of zinc chloride or dilute sulfuric acid.

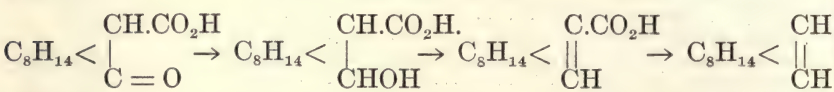
	Isoborneol	*Borneol*
Crystal form	hexagonal	hexagonal
Melting-point	212°	203°–204°
Solubility in benzene at 0°	1:2½	1:6½
Solubility in ligroin at 20°	1:2½	1:6
Phenylurethane, M.-P.	138°–139°	138°–139°
Chloral compound, M.-P.	liquid	55°– 56°
Bromal compound, M.-P.	72°	98°– 99°
Zinc chloride, conversion to	camphene	unchanged
Dil. sulfuric acid, conversion to	M.-P. 50°	unchanged
Sulfuric acid + CH_3OH	CH_3 ether	unchanged
Oxidation by CrO_3	camphor	camphor
Oxime of camphor produced, M.-P.	118°	118°
Para-nitrobenzoate [156]	129°	137°

[156] Henderson & Heilbron, *Proc. Chem. Soc.* 29, 381 (1913). The nitrobenzoate is conveniently prepared by treating with p-nitrobenzoyl chloride in pyridine.

When borneol or isoborneol is decomposed with loss of water, two hydrocarbons are produced, camphene being the principal product. The hydrocarbon formed in smaller proportions is bornylene and this hydrocarbon retains the structure of the parent alcohols.



A great deal of work has been done upon the structure of camphene and bornylene, which is reviewed elsewhere (q.v.) but in the earlier literature no distinction is made between these two hydrocarbons. Tschugaeff's method of preparing olefines by decomposing the methyl xanthate esters gives a fairly pure bornylene when applied to the decomposition of borneol.[157] Tschugaeff's bornylene melted at 109° to 109.5° and boiled at 146.5°. *Dextro*-bornylmethyl xanthate yields *lævo*-bornylene and vice versa, an interesting example of the Walden inversion. Bornylene is noteworthy for its high melting-point, as compared with all other hydrocarbons, i. e., 113°, and its boiling-point 146°. Bornylene is less readily acetylated than camphene, by the Bertram-Walbaum method. A less pure bornylene may be made by treating bornyl iodide with alcoholic caustic potash. Bornylene is also more resistant to oxidation than camphene and Henderson and Caw[158] accordingly purified bornylene by oxidation by hydrogen peroxide and obtained a specimen showing the melting-point 113° and boiled at 146°. A very pure bornylene made through camphocarbonic acid[159] also showed a melting-point of 113°, and a boiling-point of 146°.



It is still generally believed that "camphene" may be a mixture of hydrocarbons, or that camphenes of different origin are not identical. The camphenes from various natural sources differ widely in physical

[157] *Ann.* *388*, 260 (1912).
[158] *J. Chem. Soc.* *101*, 1416 (1912).
[159] Bredt, *Ann.* *366*, 11 (1909); *J. prakt. Chem.* (2) *84*, 778 (1911).

properties. Wallach[160] isolated a specimen of camphene from a Siberian pine-needle oil which showed a low melting-point, 39°, a boiling-point of 160°–161°, $d_{40°}$ 0.8555, $[\alpha]_D$ — 84.9° and $n\frac{40°}{D}$ 1.46207. Camphene made from bornylamine[161] melts at 50° and showed the high rotation of $[\alpha]_D$ 103.89°. Ordinary camphene hydrochloride, melting at 155°, is identical with the chloride of isoborneol.

Oxidation of Borneol and Isoborneol

As stated above, the old Thurlow process, practiced at Niagara Falls about 1900, employed chromic acid for oxidation of the borneols to camphor. Various special modifications of the chromic acid oxidation method have been described in the patent literature, and the processes of Verley,[162] Florizoone,[163] Ruder[164] and Weizmann[165] mention the use of a solvent added to insure thorough exposure of the borneol to the oxidizing solution. Carbon tetrachloride, benzene and acetone[165] are useful for this purpose, but acetic acid forms appreciable proportions of bornyl acetate which resist oxidation to camphor. Verley recommends 50 parts of sodium dichromate, 68 parts of sulfuric acid and 600 parts of water but Ruder employs solutions of about one third this concentration. Free sulfuric acid should be avoided as much as possible on account of the decomposition of isoborneol to camphene, which is more resistant to oxidation, by heating with dilute sulfuric acid, as noted above. Gradually acidifying the reaction mixture as the oxidation proceeds is therefore advantageous. The oxidation of camphene itself by chromic acid has been described[166] but the yields are lower than when borneols are employed. Another patentee[167] proposed to employ potassium persulfate for the oxidation of camphene. The use of sodium dichromate or chromic acid for this purpose, on a tonnage scale, involves the electrolytic regeneration[168] of this oxidizing material or its utilization as basic chromium salt solutions in tanning or the mordanting of textile goods, otherwise the method would be too costly.

[160] *Ann.* *357*, 79 (1907).
[161] Wallach, *Ann.* *357*, 84 (1907).
[162] U. S. Pat. 908,171 (1908).
[163] Brit. Pat. 5,513 (1908).
[164] U. S. Pat. 1,066,758 (1913).
[165] Brit. Pat. 21,946 (1907).
[166] Dubosc, Brit. Pat. 8260-A (1906); 8356-A (1906).
[167] Sauvage, French Pat. 389,092.
[168] Ges. Chem. Ind. Basel,—French Pat. 387,539; LeBlanc, *Z. Elektrochem.* 7, 290 (1900); McKee & Leo, *J. Ind. & Eng. Chem.* *12*, 16 (1920).

The yields of camphor by oxidizing the borneols by air, in the absence of catalysts, are very poor,[169] but catalytic dehydrogenation of borneol to camphor, by means of finely divided copper[170] at 175°–180° or reduced nickel[171] at 200°–240° is said to have been practiced industrially. Aloy and Brustier[172] state that when borneol is passed over copper at 300° the yield of camphor is quantitative but that above 320° the yield of camphor is progressively diminished until at 420° hydrocarbons only are produced. Camphor is not reduced to borneol by hydrogen and catalytic nickel at 180°–200°, either alone or in solution in cyclohexanol. Neave[173] states that borneol yields camphor in nearly quantitative yields by passing over finely divided copper at 300° but that isoborneol under the same conditions gives chiefly camphene. Thorium oxide at 350° yields a terpene mixture boiling at 150° to 180°, the constituents of which were not definitely characterized.[174] Small proportions of unchanged bornyl chloride or other chlorides poison the catalyst unless the material is previously purified to remove such chlorides, as, for example, by digesting with a little inert solvent over metallic sodium.

Quite a number of processes for the oxidation of the borneols by nitric acid or oxides of nitrogen have been described. Hesse[175] used pure concentrated nitric acid; another process[176] prescribes nitric acid containing oxides of nitrogen, at 10° to 15°, and nitrous acid itself is said to give excellent yields.[177] The addition of small amounts of vanadium pentoxide to the nitric acid is claimed to be advantageous and several patents have recently been granted to Andreau,[178] who employs a mixture of about 339 parts of sulfuric acid 66° Bé, and 253 parts of nitric acid, 26° Bé, and who notes that once the oxidation has been initiated by raising the temperature to about 40°, the reaction may then be carried out smoothly with cooling so that the temperature does not rise above 40°. In the nitric acid process the camphor forms a liquid double compound with the nitric acid, which floats on the acid mixture as a sparingly soluble oil layer. This obviates the use of a solvent to insure complete oxidation of the

[169] Cf. Stephan & Rehlander, U. S. Pat. 801,485.
[170] Schering, German Pat. 161,523; Goldsmith, Brit. Pat. 17,573 (1906).
[171] Aschan & Kempe, U. S. Pat. 994,437 (1911); Zimmerman, Brit. Pat. 26,708 (1904).
[172] *Bull. soc. chim.* (4) *9,* 733 (1911).
[173] *J. Chem. Soc. 101,* 513 (1912).
[174] Aloy & Brustier, *J. pharm. chim.* (7) *10,* 49 (1914).
[175] *Ber. 39,* 1144 (1906).
[176] Ges. Chem. Ind. Basel, Brit. Pat. 9,857 (1907); Philip, Austrian Pat. 33,720 (1908).
[177] Boehringer & Son, U. S. Pat. 802,793 (1904).
[178] U. S. Pat. 1,347,071 (1920).

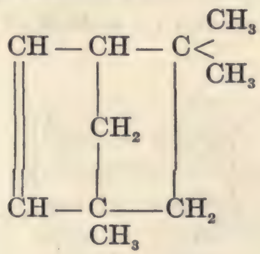
borneol, enclosure of borneol particles by solid camphor being avoided. The oily nitric acid compound is decomposed by water, precipitating the camphor. Camphoric acid and nitrocompounds are also formed, the latter coloring the crude camphor light yellow, and imparting to it a peculiar "nitro" odor.

Practically every known method of oxidizing organic compounds has been proposed for the oxidation of the borneols, or camphene, to camphor, including chlorine,[179] hypochlorites,[180] potassium permanganate both in acid [181] and alkaline [182] solution, etc. When permanganate is employed the camphor formed is removed from the spent mixtures by distilling with steam. Camphene, in dilute acetone, has also been oxidized by potassium permanganate, to camphor.[183] All of these methods using permanganate are relatively very costly, except where methods for its regeneration have been perfected.

Impurities of Crude Synthetic Camphor

If the borneol or isoborneol is not purified before oxidation, the resulting camphor will contain small proportions of the fenchones, which, like camphor, are quite resistant to further oxidation and form very stable double compounds with nitric acid.

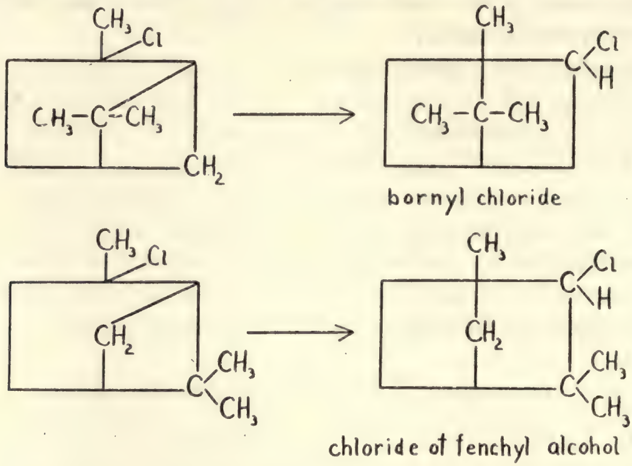
The behavior of the fenchenes in the Bertram-Walbaum reaction follows the general esterification behavior of unsaturated terpenes. Komppa and Hinticka [184] share Quist's view that isofenchene, boiling-point 152°–155° has the constitution.



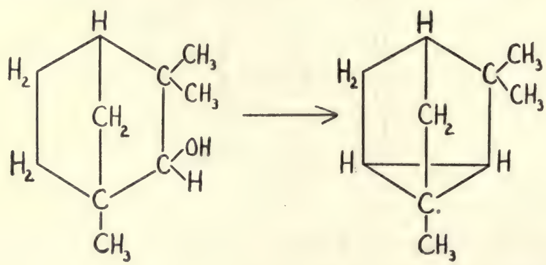
As noted above the chief impurity in bornyl chloride is dipentene dihydrochloride but fenchyl chloride is present in the oily part of the

[179] Boehringer & Son, U. S. Pat. 802,792; Brit. Pat. 28,035 (1904).
[180] Hertkorn, U. S. Pat. 901,708 (proposes the addition of salts such as $CuCl_2$ and $FeCl_3$); Glaser, U. S. Pat. 875,062; 864,162 (1907).
[181] Semmler, *Ber. 33,* 3430 (1900).
[182] Schering, German Pat. 157,590 (1903); Stephan and Hunsalz, U. S. Pat. 770,940 (1904).
[183] Behal, Austrian Pat. 38,203 (1908).
[184] *Chem. Abs. 13,* 2864 (1919).

hydrochloride mixture since fenchene has been found in the crude camphene made from these chlorides. Aschan[185] represents the formation of bornyl chloride and fenchyl chloride as follows,



Crude camphene also contains a very small amount of β-pinolene or tricyclene. It will be noted that the fenchyl chloride or the corresponding alcohol whose structure is shown above cannot lose HCl or water to form a double bond with either of the adjacent carbon atoms. But Quist made tricyclene by decomposing the methyl xanthate ester of fenchyl alcohol and therefore shares Aschan's views as to the nature of tricyclene and its method of formation,

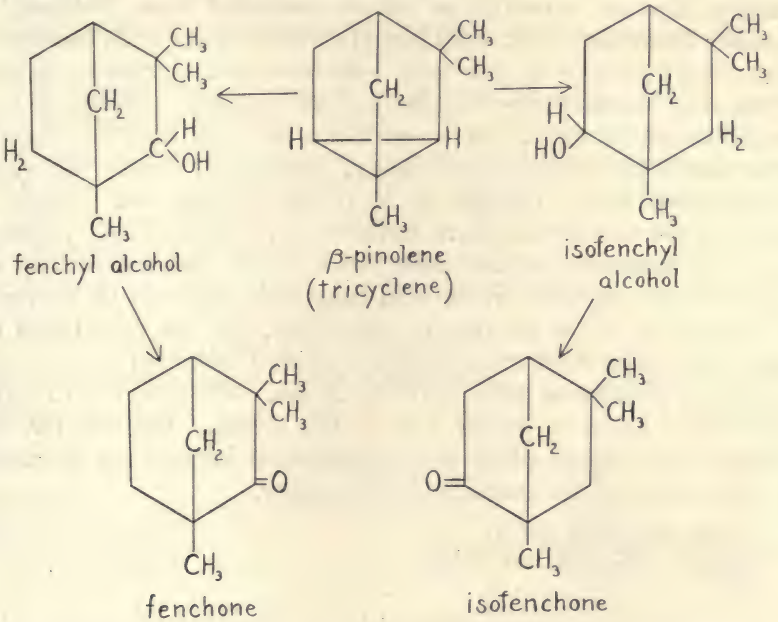


Tricyclene is stable toward alkaline permanganate but, as with most cyclopropane structures, acids rupture the 3 carbon ring and the Bertram-Walbaum reaction accordingly gives the acetate of isofenchyl alcohol. Hydrogen chloride at —10° yields a hydrochloride

[185] *Ann.* 387, 24 (1912).

melting at 27.5° to 29°, which on decomposition forms a fenchene boiling at 154°. Tricyclene itself, as purified by Aschan by oxidizing the accompanying fenchenes by permanganate, boils at 141.5°–143.5.°

Fenchenes or tricyclene contained in the crude camphene, employed for the manufacture of artificial camphor, will accordingly be converted to fenchyl and isofenchyl alcohols which will in turn be oxidized to the corresponding ketones. The relations of these substances are probably as follows,



As regards the purification of synthetic camphor for industrial purposes, it should be noted that manufacturers of celluloid usually specify that the chlorine [186] content shall not exceed 0.1% and borneol should not be present in excess of 0.5 per cent. For some grades of celluloid a melting-point of 165° is sufficient but for high-grade material the melting-point should not be lower than 174°. A saturated solution in 95 per cent alcohol should show no yellow color and when kept in ordinary diffused daylight in a colorless transparent bottle the

[186] For the quantitative determination of chlorine in synthetic camphor the method of Drogin and Rosanoff (*J. Am. Chem. Soc.* 38, 711 [1916]), or that of Van Winkle and Smith (*J. Am. Chem. Soc.* 42, 333 [1920]) is recommended. The per cent. of borneol may be determined by acetylating with acetic anhydride, in the usual manner, and determining the saponification number of the product; borneol or isoborneol may also be separated from camphor by the phthalic anhydride method.

camphor should not become visibly discolored in 30 days. Nitro derivatives are very apt to cause the development of a yellow color. The presence of nitro derivatives also causes the formation of a slight tarry or resinous residue when a few grams of the camphor are sublimed slowly from a watch glass. The chief impurities encountered in commercial natural camphor are camphor oil, water and mineral matter.

As regards the yields of synthetic camphor obtained in industrial practice there are naturally no reliable published data. Schmidt[187] gives the following yields: solid bornyl chloride 43 per cent, camphene from bornyl chloride 95 per cent, isobornyl acetate from camphene 86 per cent, saponification to isoborneol 98 per cent, oxidation of isoborneol to camphor about 80 per cent, or a net yield from the original turpentine of 24 per cent of the theory. Austerweil[188] gives the yield of crystalline bornyl chloride as 55 to 60 per cent and Ullman[189] gives 55.3 per cent of the theory as the yield of the chloride. According to the writer's experience these yields are too low, particularly as regards bornyl chloride, which with reasonable skill can be obtained in yields of 75 to 78 per cent of the theory, and the acetylation of camphene can be relief upon to give a yield of isobornyl acetate corresponding to 92 to 94 per cent of the theory. The net yield of camphor should be 45 to 50 per cent of the theory. Methods for the synthesis of camphor which are of theoretical interest are discussed in connection with the constitution of camphor.

[187] *Chem. Ind. 29,* 241 (1906).
[188] German Pat. 211,799 (1908).
[189] *Enzykl. techn. chem.* III, 257.

Chapter XIV. Cyclic Non-benzenoid Hydrocarbons.

Cycloheptane, Cyclooctane, Cyclononane and Polynaphthenes.

Cycloheptane and its derivatives are difficult to prepare and have been comparatively little studied. The ketone, cycloheptanone (suberone), is the material most frequently employed for the preparation of other cycloheptane derivatives and Willstätter has used the cycloheptatriene (tropilidene) formed by the exhaustive methylation and decomposition of tropidine, and also cycloheptatriene from anhydro-ecgonine. Eucarvone has also been employed in the preparation of other cycloheptane derivatives.

The physical properties of cycloheptane, cycloheptene, cycloheptadiene (hydrotropilidine) and cycloheptatriene (tropilidine) are as follows,[1]

	Boiling-Point	$\frac{0°}{d\,0°}$	n_D
Cycloheptane	117. °–117.5°	0.8253	....
Cycloheptene	114.5°–115. °	0.8407	....
$\Delta^{1,3}$-cycloheptadiene	120. °–121. °	0.8810	1.495997
$\Delta^{1,3,5}$-cycloheptatriene	116. ° (corr.)	0.9083	1.5175

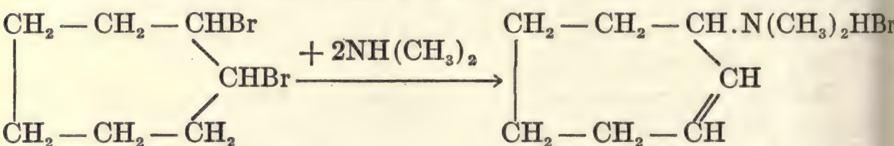
Cycloheptane was made by Markownikow[2] from cycloheptanone by reducing the ketone to cycloheptanol (suberyl alcohol) and reducing the corresponding bromide by zinc dust and alcohol. Willstätter and Kametaka[3] reduced cycloheptadiene (hydrotropilidene) by Sabatier and Senderens' method, at 180°. The cycloheptane made under these conditions is quite pure but at 235° further hydrogenation to normal heptane occurs and at 250° this change is quite rapid. Cycloheptanol cannot be reduced to cycloheptane by heating with hydriodic acid, methylcyclohexane being formed.[4]

The formation of a hydrocarbon, C_7H_8, by distilling methyltropine-

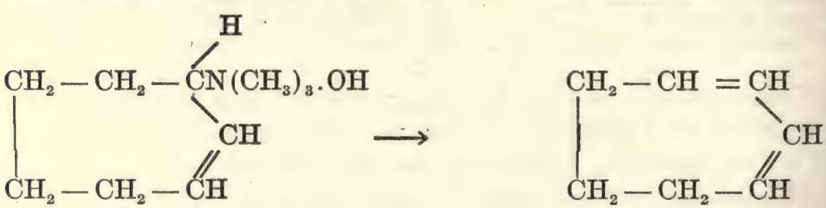
[1] Willstätter, *Ann.* *317,* 204 (1901).
[2] *Ann.* *327,* 59 (1903).
[3] *Ber.* *41,* 1480 (1908).
[4] Markownikow, *J. prakt. Chem.* (2) *49,* 430 (1894).

methyl iodide was observed by Ladenburg, and Merling[5] obtained the hydrocarbon by exhaustive methylation of tropidine and decomposing the tertiary ammonium hydroxide by heat. The conversion of tropinic acid to normal pimelic acid led to the view that the tropine bases and their nitrogen free decomposition products possessed a cycloheptane ring and that tropilidine and hydrotropilidine were cycloheptatriene and cycloheptadiene respectively. Willstätter confirmed this by synthesizing both hydrocarbons.

Cycloheptene can readily be prepared by decomposing cycloheptyl iodide in the usual manner, and the addition of bromine gives 1.2-dibromocycloheptane, but when the dibromide is heated with quinoline two bromine atoms are removed, not two molecules of hydrobromic acid, the resulting product being cycloheptene, not the *expected diene.* Alcoholic caustic potash converts the dibromide into the unsaturated ether, and similarly, heating the dibromide with dimethyl amine forms a dimethyl amino derivative,

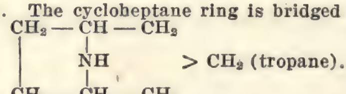


By adding methyl iodide to the resulting base and decomposing the tertiary ammonium hydroxide by heat, Willstätter made $\Delta^{1.3}$-cycloheptadiene, which proved to be identical with hydrotropilidene



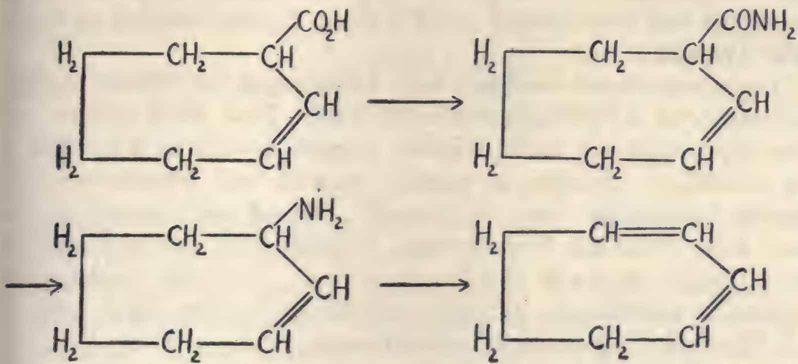
Willstätter also made $\Delta^{1.3}$-cycloheptadiene in another manner.[6] From the decomposition products of cocain Δ^{1}-cycloheptenecarboxylic acid was obtained, which was treated with hydrogen bromide to form 2 bromocycloheptanecarboxylic acid, which was decomposed, losing

[5] *Ber.* *24*, 3109 (1891). The cycloheptane ring is bridged in the following manner,

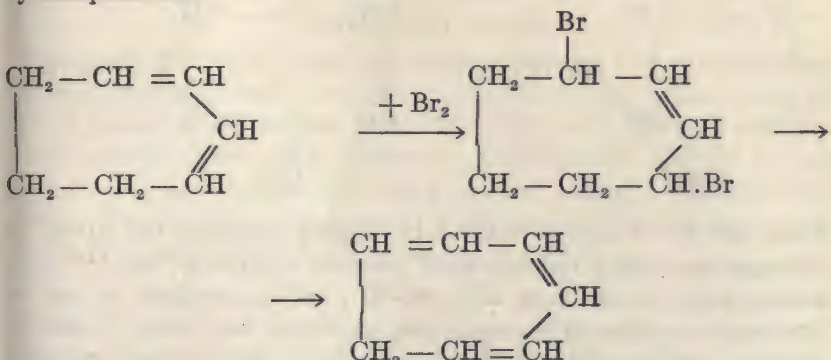


[6] Einhorn & Willstätter, *Ann.* *280*, 136 (1894).

HBr to form a mixture of the Δ^1 and Δ^2 acids. The Δ^2 acid was separated by fractional crystallization, converted to the amide, and the latter treated with bromine and alkali (Hofmann's reaction) to form the amine, from which, by the method of exhaustive methylation, the conjugated diene was made.



The addition of bromine to $\Delta^{1.3}$-cycloheptadiene takes place in accordance with the general rule of the addition of bromine to conjugated dienes, to form 1.4-dibromo-Δ^2-cycloheptene, which by heating with quinoline, loses 2 molecules of hydrogen bromide to form cycloheptatriene



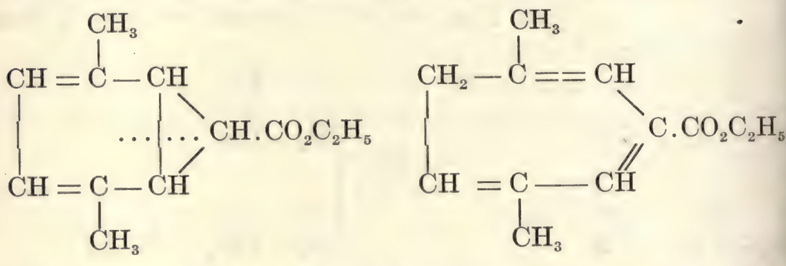
Cycloheptatriene resinifies rapidly in contact with the air and follows generally the behavior of conjugated dienes.

Tetramethylcycloheptatriene was made by treating eucarvone with magnesium-methyl iodide.[7] It is not definitely known whether the

[7] Rupe & Kerkovius, *Ber.* 44, 2702 (1911).

third double bond is in the ring or semicyclic. The physical properties of the hydrocarbon are as follows, boiling-point 67°–67.5° (11 mm.), $d_{20°}$ 0.8687, n_D 1.5066, M_D 50.70, EM_D 1.33. Its constitution may be inferred from the constitution of eucarvone (q.v.). It is very little changed by boiling with 10 per cent sulfuric acid. Reduction by sodium and ethyl alcohol yields a diene, $C_{11}H_{18}$, distilling at 64.5°–65.5° (12 mm.).

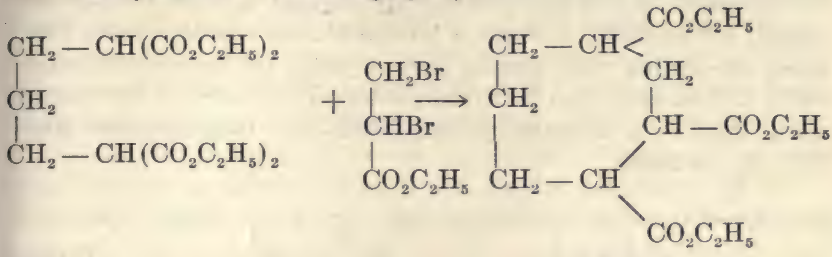
Diazoacetic ester combines with toluene and the xylenes to form derivatives of norcaradienecarboxylic acid. Thus when toluene and diazoacetic ester are boiled together (copper powder as a catalyst is not necessary) nitrogen is rapidly evolved and 3-methylnorcaradienene-7-carboxylic ester is formed. Para-xylene, treated in the same way, yields the bicyclic ester, and this ester can be treated in several ways to break the 3-carbon ring. The first condensation product is regarded by Buchner and Schulz [8] as the ethyl ester of 2.5-dimethyl-$\Delta^{2.4}$-norcaradienenecarboxylic acid. By heating the amide to 160°–170°, or heating the crude condensation product with 15 per cent sulfuric acid, or by heating with water at 160°–170°, the 3-carbon ring is broken, forming chiefly 2.5-dimethyl-$\Delta^{2.5.7}$-cycloheptatriene-7-carboxylic acid, melting-point 136°–137°.



When the $\Delta^{2.5.7}$ acid is reduced by sodium amalgam two atoms of hydrogen are added forming what Buchner regards as the $\Delta^{2.5}$ acid, melting-point of the crude acid 38°–40°, but too unstable to purify. Obviously a number of isomeric acids containing two double bonds are possible, and by adding hydrogen bromide to the $\Delta^{2.5}$ acid and then removing HBr by the action of alkali, Buchner obtained an isomeric acid melting at 82°, which he regards as the $\Delta^{2.6}$ acid. Reduction by hydrogen and platinum black yields 2.5-dimethylcycloheptanecarboxylic acid, an oil at ordinary temperatures (amide melting at 185°–186°).

[8] *Ann.* 378, 259 (1910).

Goldsworthy and Perkin[9] made *trans.* 1.2.4.-cycloheptanetricarboxylic acid by the latter's well-known method of synthesis, using sodium ethylate as a condensing agent,



The ester was saponified by alcoholic caustic potash in the usual manner, the free acid melting at 198°–200°.

Cycloheptanone, the raw material most frequently employed for preparing cycloheptane derivatives, may be prepared by heating the calcium salt of suberic acid.[10] When purified by means of the semicarbazone or the bisulfite compound and regenerating the ketone, it has the following physical properties, boiling-point 180°, $d\frac{21.5°}{4°}$ 0.9498, n_D 1.46027, M_D 32.35 (calculated 32.34).[11]

Cycloheptanone forms a dibenzylidene derivative,

$$C_7H_8O.(CH.C_6H_5)_2,$$

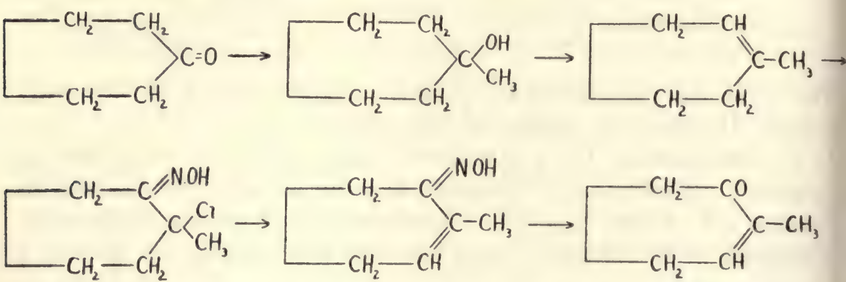
melting at 107°–108°, and like cyclopentanone and cyclohexanone, forms a series of well crystallized compounds with other aldehydes (with anisaldehyde, melting-point 128°–129°; with cinnamic aldehyde, melting-point 198°; with piperonal, melting-point 137°). It condenses with acetone but with much greater difficulty than the lower cyclic homologues.[12] Like other cyclic ketones the oxime is rearranged by sulfuric acid to the so-called isooxime,

$$\begin{array}{l} CH_2 - CH_2 - CH_2 - CO \\ | \qquad\qquad\qquad\qquad\quad | \\ CH_2 - CH_2 - CH_2 - NH \end{array}$$

This isooxime is readily split by heating with hydrochloric acid to amido-n-heptylic acid. The ketone reacts normally in the Grignard reaction, for example, with magnesium-methyl iodide to form 1-meth-

[9] *J. Chem. Soc.* *105*, 2675 (1914).
[10] Wislicenus & Mager, *Ann.* *275*, 357 (1893).
[11] Auwers, *Ann.* *410*, 283 (1915).
[12] Wallach, *Ann.* *394*, 366 (1913).

ylcycloheptanol-(1), which in turn readily decomposes to Δ^1-*methylcycloheptene*, boiling-point 137.5°–138.5°, $d_{19.5°}$ 0.824, n_D 1.4581. The reactions of this hydrocarbon are parallel to those already discussed; for example, it forms a nitrosochloride (melting-point 106°) which on heating with dimethylaniline yields the unsaturated oxime which in turn may then be hydrolysed by dilute acids to the unsaturated ketone Δ^1-2-methylcycloheptene-3-one (boiling-point 200°–205°, $d_{21°}$ 0.9695).



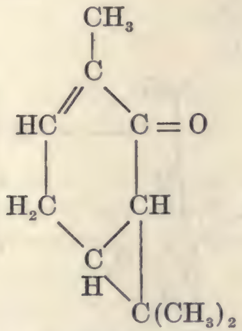
It also condenses with bromo-acetic ester in the presence of zinc to give cycloheptanol acetic acid, from which Wallach [13] obtained methenecycloheptane in the usual manner. *Methenecycloheptane* distills at 138°–140°, $d_{20°}$ 0.824, n_D 1.4611. This hydrocarbon undergoes reactions strictly parallel with those which have already been discussed in connection with other hydrocarbons having the methene $>C=CH_2$ group, for example, on oxidation it forms a glycol (melting-point 50°–51°) which is converted to cycloheptane aldehyde by heating with dilute acids.

Kötz [14] has studied the chlorination and bromination of cycloheptanone and finds that, like cyclohexanone, the halogen enters the ring in the CH_2 group adjacent to the carbonyl group, these facts harmonizing with the view that the ketone reacts with the halogen in the enol form, adding Cl_2 or Br_2 and subsequently splitting off a molecule of halogen acid. The chloroketone is much more stable than the bromoketone. The chloroketone is not hydrolyzed by aqueous caustic potash at ordinary temperatures but, on warming, the corresponding oxyketone is formed (yield poor). Oxyketones of this type show most interesting properties; neither the oxyketone nor its methyl ether forms an oxime and the methyl ether may readily be prepared by

[13] *Ann.* *314*, 158; *345*, 146.
[14] *Ann.* *400*, 47 (1913).

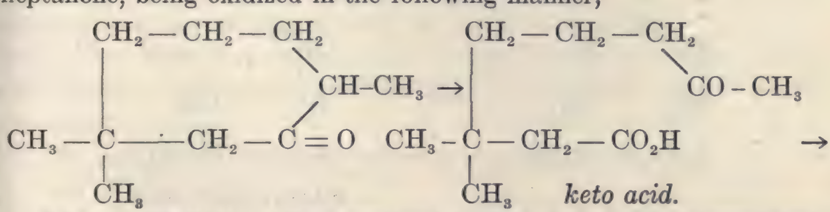
saturating the methyl alcohol solution by hydrogen chloride, like the esterification of a carboxylic acid. The unsaturated ketone, Δ^2-cycloheptenone, was reduced by Kötz, by Paal's method, to cycloheptanone, confirming Willstätter's[15] constitution for this ketone (tropilene).

Eucarvone: When carvone combines with one molecule of hydrobromic acid and is then treated with alkali to remove HBr, the resulting ketone proves to be an isomer of carvone. Baeyer, the discoverer of the reaction, regarded eucarvone as bicyclic having a cyclopropane ring although he himself pointed out several objections to such a structure. Dihydroeucarvone and tetrahydroeucarvone he regarded as derivatives of cycloheptanone. Further objections to Baeyer's constitution for eucarvone



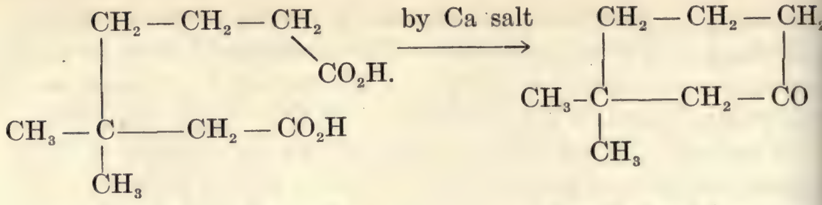
eucarvone (Baeyer)

were pointed out by Wallach, who prepared a condensation product with benzaldehyde, clearly indicating the presence of the $—CH_2—CO—$ group. Also, when prepared from optically active carvone, eucarvone, according to Baeyer's constitution, should be capable of optical activity, but, as Baeyer himself observed, it is inactive. Reduction of eucarvone by sodium gives dihydroeucarvone and a little tetrahydroeucarvone, but by catalytic hydrogenation in the presence of palladium tetrahydroeucarvone is readily produced,[16] a method of reduction which practically precludes rearrangements. Baeyer had already shown that tetrahydroeucarvone was a derivative of cycloheptanone, being oxidized in the following manner,



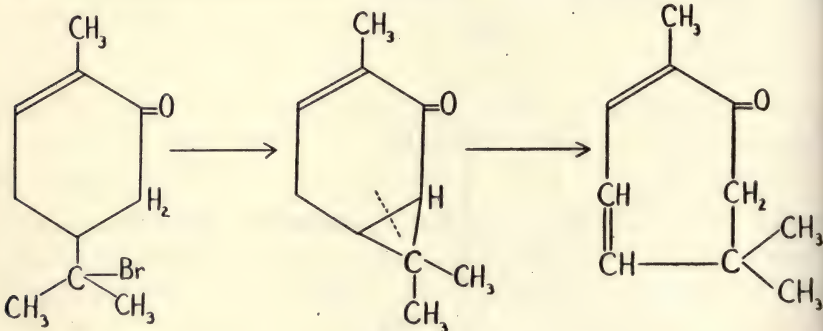
keto acid.

[15] *Ber. 44*, 465 (1911). Others considered tropilene to be tetrahydrobenzaldehyde.
[16] Wallach, *Ann. 339*, 107; *381*, 67.



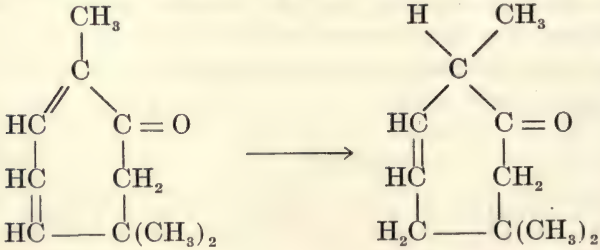
ββ-*dimethylpimelic acid* *dimethylcyclohexanone.*

Wallach therefore explains the behavior of eucarvone by the following formula, the bicyclic ketone assumed by Baeyer evidently being an unstable intermediate product,



hydrobromocarvone *unstable intermediate product* *eucarvone* (Wallach)

The reduction by sodium indicates that the two double bonds in eucarvone are in the conjugated position, but the constitution of the dihydro derivative is not definitely known, although the reduction probably follows the partial valence rule of Thiele, leading to the following constitution for dihydroeucarvone.



dihydroeucarvone?

Eucarvone has the following physical properties, boiling-point 85°–87° (12 mm.); $d_{20°}$ 0.952, $n\frac{20°}{D}$ 1.5048.[18] Its semicarbazone melts at 183°–185°, the oxime at 106° and the benzylidene compound, formed by its reaction with benzaldehyde, melts at 112°–113°. By partially hydrogenating the oxime of eucarvone Wallach[19] discovered the oxime of a dihydroeucarvone, which is not identical with that previously known, and Wallach accordingly distinguishes the two known dihydroeucarvones as α and β, the latter being the newly discovered one.

	B. P.	*d* *21°*	*Oxime* *M. P.*	*Semicarbazone* *M. P.*
α	205°	0.9215	liquid	189°–191°
β	213°–214°	0.9325	122°–123°	195°–197°

Tetrahydroeucarvone has the following physical properties, boiling-point 207°, $d_{20°}$ 0.906, n_D 1.4553; it yields a semicarbazone, obtained in two forms one melting at 201° and the other at 161°–163°; the oxime is an oil when made from the saturated ketone but when made by the catalytic hydrogenation of eucarvoxime, melts at 56°–57°, the further reduction of which yields tetrahydroeucarvylamine.

Cyclooctane: Just as tropin may be oxidized to tropinic acid and to normal pimelic acid, pseudopelletierin may be oxidized to suberic acid. The alkaloid from pomegranate root therefore contains a cyclooctane ring, in fact, as Ciamician and Silber,[20] and Piccinini[21] have shown, the alkaloid contains the bridged ring

$$\begin{array}{ccccc} CH_2 & \text{———} & CH & \text{———} & CH_2 \\ | & & | & & | \\ CH_2 & & N.CH_3 & & CO \\ | & & | & & | \\ CH_2 & \text{———} & CH & \text{———} & CH_2 \end{array}$$

By exhaustive methylation of the base, adding methyl iodide to *des*-dimethylgranatanine and decomposing the free tertiary ammonium hydroxide, Willstätter and Veraguth[22] obtained a cyclooctadiene. The octadiene polymerizes so readily that when distillation was attempted polymerization occurred at 130°–150°, with almost

[18] Wallach, *loc. cit.*
[19] *Goett. Nachr. 1913,* 246.
[20] *Ber. 26,* 156, 2738 (1893); *27,* 2850 (1894); *29,* 490, 2970 (1896).
[21] *Gazz. chim. Ital. 29* (2), 104 (1899).
[22] *Ber. 38,* 1976 (1905).

explosive violence, to a resinous mass and resinification takes place rapidly on standing in contact with air. At 16.5 mm. it distills at 39.5°, d $\frac{0^\circ}{4^\circ}$ 0.889. It has a very penetrating, unpleasant odor and inhalation of the vapors readily produces headache. It reacts readily with nitric acid, dissolving completely. On standing the hydrocarbon is converted to a dimeride which may be crystallized out by strongly cooling, the crystals melting at 114°. Bromine reacts with the hydrocarbon very energetically even at — 10° in chloroform solution, some hydrobromic acid being evolved. When the dihydrobromide is decomposed by heating with caustic alkali or quinoline, a new octadiene is formed, distilling at 143°–144° and characterized by a very pleasant odor, and almost no tendency to polymerization. The former cyclooctadiene has properties very strikingly similar to those of cyclopentadiene and Willstätter accordingly regards the first diene as having the double bonds in conjugated positions, i. e., $\Delta^{1.3}$-cyclooctadiene. The more stable cyclooctadiene, evidently $\Delta^{1.4}$ or $\Delta^{1.5}$, is smoothly reduced by Sabatier and Senderen's method to *cyclooctane,* boiling-point 146.3°–148°. Cyclooctane is stable to permanganate but is oxidized by nitric acid to suberic acid.

When the unstable diene, α-cyclooctadiene, is treated with hydrobromic acid, the dihydrobromide formed is always accompanied by a *saturated* monohydrobromide, from which a bicyclic octene is formed by heating with quinoline. This bicyclic hydrocarbon distills at 138°–139°, d $\frac{0^\circ}{4^\circ}$ 0.9097. Its constitution is not definitely known; by carefully oxidizing with permanganate a crystalline α-oxyketone is formed, $C_6H_{10}\!<\!\begin{array}{l}CO\\|\\CHOH.\end{array}$

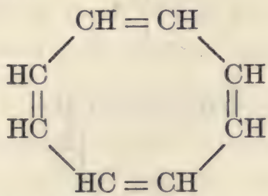
The yield of cyclooctanone obtained by heating the calcium salt of azelaic acid is very poor. The ketone distills at 195°–197°, melting-point 25°–26°.

By distilling the barium salt of β-vinylacrylic acid Doebner[23] has obtained a cyclooctadiene boiling at 50°–52° (17 mm.) which he regards as $\Delta^{1.5}$-cyclooctadiene. Sorbic acid treated in the same way yields 3.4-dimethyl-$\Delta^{1.5}$-cyclooctadiene, boiling-point 68°–71° (15 mm.).

By decomposing the tetrabromide of the more stable or β-cyclo-

[23] *Ber.* 35, 2129 (1902); *Ber.* 40, 146 (1907).

octadiene, Willstätter[24] obtained cyclooctatetrene. Cyclooctatetrene has been of interest because of the fact that it possesses none of the properties characteristic of the benzenoid hydrocarbons. It readily combines with 4 molecules of hydrogen, reduces permanganate and absorbs bromine. With nitric and sulfuric acid nitrating mixtures, it yields resin but no nitro-derivatives. Its structure is therefore to be represented as follows:



Willstätter, who discovered the substance, accordingly states that benzene cannot have the structures indicated by the Kekulé constitution. No indication of the existence of a more stable form was obtained and Willstätter, favoring the Armstrong and Baeyer constitution for benzene, considers that in the case of an eight carbon ring centric equilibrium of the fourth valence of each carbon atom is not established because the distance of the carbon atoms from the center, or from opposite carbon atoms, is greater than in the case of benzene.

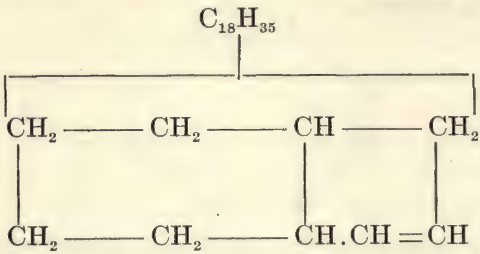
As might be surmised from the properties of the fulvenes, noted above, cyclooctatetrene is a *yellow* oil of very powerful odor, oxidizes rapidly in contact with air and readily polymerizes.

Cyclononane: Calvi[25] attempted to prepare cyclononanone by heating the calcium salt of sebacinic acid but without success, and later Petersen[26] attempted the same preparation but noted a very complex decomposition, identifying benzene, propionic aldehyde and heptane aldehyde among the products. Dale and Schorlemmer[27] noted the formation of a hydrocarbon $C_{16}H_{32}$ distilling at 283°–285°, under similar conditions. Zelinsky[28] obtained only 20 grams of a ketonic substance from 2 kilos of sebacinic acid, from which he prepared the semicarbazone and regenerated the ketone in the usual manner. The ketone distills at 95°–97° (17–18 mm.), $d \frac{22.5°}{4°} 0.8665$. Zelinsky reduced the ketone, with sodium and moist ether, to the alcohol which he converted to the iodide and reduced the latter by

[24] Willstätter & Waser, *Ber.* *44*, 3423 (1911).
[25] *Ann.* *91*, 110 (1854).
[26] *Ann.* *103*, 184 (1857).
[27] *Ann.* *199*, 149 (1879).
[28] *Ber.* *40*, 3278 (1907).

zinc dust in acetic acid. The quantity of the hydrocarbon made by Zelinsky was evidently too small for great reliance to be placed upon its physical constants and inferences drawn therefrom.

According to Windaus [29] cholesterol contains a bicyclic nine carbon atom ring, having obtained evidence of a ring of the character indicated by the following partially elucidated formula,



Polynaphthenes: Lubricating oils of the general empirical formula C_nH_{2n-2} and C_nH_{2n-4} are generally believed to be polycyclic hydrocarbons although there is no direct evidence of their constitution other than the empirical formula and inferences drawn from their physical properties such as viscosity and their not crystallizing at low temperatures. Such oils, even when repeatedly distilled and fractions separated within very narrow temperature limits, are undoubtedly very complex mixtures and the great difficulty of separating pure substances from even simpler mixtures has already been pointed out. The task of determining the constitution of such hydrocarbons, assuming it to be worth while, would be an almost impossible one and probably not worth the enormous effort required.

When formaldehyde or para-formaldehyde is heated with tetrahydronaphthalene and phosphorus pentoxide, a highly viscous oil is obtained, boiling at 257°–258° (15 mm.). A brittle resin is also formed. The oil has been proposed as a lubricant and its process of manufacture patented.[30] Heusler and Engler [31] observed the polymerization of light, low-boiling, unsaturated hydrocarbons to polynaphthenes of the lubricating oil type, by heating the former hydrocarbons under pressure. It is quite possible that the lighter unsaturated hydrocarbons found in shale oil distillates could be polymerized by such a process,[32] or by treating with anhydrous aluminum chloride, to more stable polymers of the lubricating oil type; in fact, such a

[29] *Ber.* *53*, 488 (1920).
[30] German Pat. 333,060; 319,799.
[31] *Ber.* *28*, 490 (1895); *30*, 2358, 2365 (1897).
[32] Phenols and organic acids present in crude shale oil naturally destroy the efficacy of the aluminum chloride, unless removed.

process, using aluminum chloride, has already been carried out industrially in the United States, polymerizing the low-boiling olefines made by cracking (such olefines being largely lost by the usual refining process), to lubricating oils of good quality.

In the absence of scientific information regarding the chemical constitution of lubricating oils, a great many claims are sometimes made for the supposed excellence of certain oils, or rather commercial brands. As pointed out by Dunstan and Thole [33] "It appears beyond doubt that the high boiling fractions of petroleum, irrespective of their place of origin, are complex mixtures containing a very small percentage of paraffine hydrocarbons of the formula C_nH_{2n+2}, and consisting chiefly of compounds whose formulæ range from C_nH_{2n} to C_nH_{2n-8}." This is true even of so-called paraffine base oils of the light Pennsylvania type.

The nature of the unsaturated hydrocarbons in lubricating oils is an open question. They show large losses on treating with concentrated sulfuric acid, these losses amounting to 20 to 40 per cent; they show indefinite iodine numbers but attempts to hydrogenate such oils have been negative. Treatment with liquid sulfur dioxide results in a partial separation. Thus, an oil showing an iodine number of 46 gave, after extraction, a residue of iodine number 33 and an extracted portion having an iodine number of 73. Somewhat similar results are effected by fullers' earth.

As previously pointed out, the usual methods of determining iodine numbers are of little value for lubricating oils. Thus Dunstan and Thole state that the reaction of mineral oils toward iodine differs profoundly from that of fatty oils. According to their experience with the Wijs reagent, by varying the time and proportion of iodine chloride, a given mineral oil may yield widely varying values. For example, a California mineral oil gave a value of 20 in 2 hours, 40 in 4 hours, 60 in 64 hours and 80 in 266 hours, whereas rape oil reached a steady value in three minutes. Again, the iodine value of rape oil was found to be practically independent of the amount of Wijs' solution used (provided a fair excess was employed) but with a mineral lubricating oil an increase in the proportion of reagent to oil invariably augments the iodine value.

Highly refined oils such as white pharmaceutical oil are inferior in viscosity and lubricating value to those oils which are less highly refined and which contain a certain proportion of so-called unsaturated hydrocarbons.

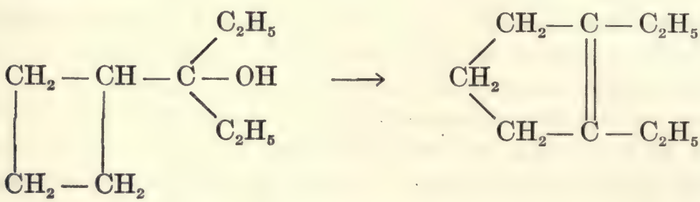
[33] *J. Inst. Petr. Techn.* 7, 417 (1921).

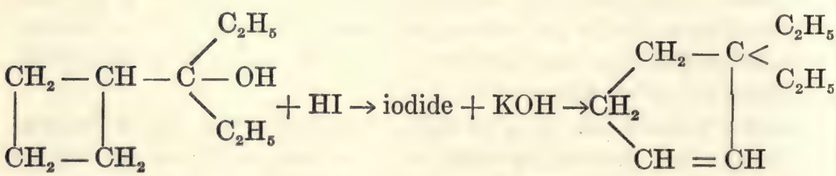
Chapter XV. Rearrangements

Rearrangement of carbocyclic structures to substances having a different number of carbon atoms in the ring is occasionally observed in the case of hydrocarbons but such rearrangements are much more frequently noted with derivatives.

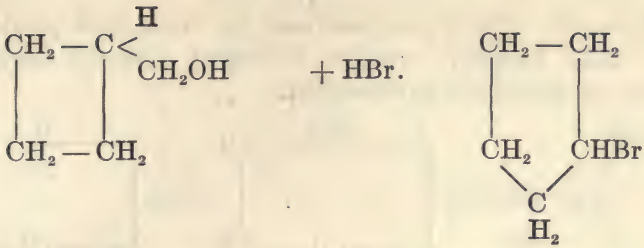
On strongly heating cyclohexane under pressure, conversion to methylcyclopentane occurs and Markownikow[1] showed that when cyclohexyl chloride or iodide is heated with concentrated hydriodic acid methyl cyclopentane is formed. Pure cyclohexane, however, is not effected by heating with hydriodic acid. The conversion of cycloheptyl iodide into methylcyclohexane and dimethylcyclopentane is a reaction of very much the same kind. Cyclobutylcarbinol and hydrogen bromide results in conversion of the four carbon to the five carbon ring, namely, to cyclopentylbromide.

Change of cyclobutane derivatives to cyclopentane derivatives was noted by Kishner[2] on heating dimethyl or diethylcyclobutyl carbinol with oxalic acid.

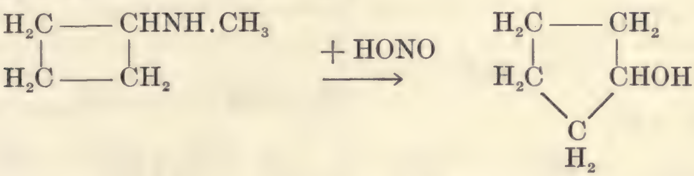




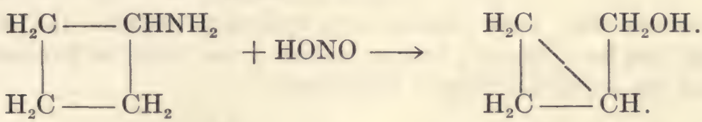
[1] *Ann.* **302**, 1 (1898).
[2] *J. Russ. Phys.-Chem. Soc.* **42**, 1211 (1910); **43**, 1149 (1911).



The change of the four carbon ring in pinene to a five carbon ring by the action of dry hydrogen chloride forming bornyl chloride is a reaction the mechanism of which is obscure, but is, nevertheless, an illustration of the tendency of four carbon atom rings to rupture or to change to five carbon atom rings. Demjanow[3] discovered that cyclobutylmethylamine is converted into cyclopentanol by the action of nitrous acid:

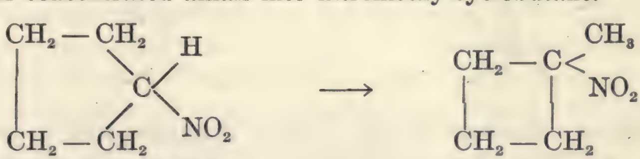


Cyclobutylamine and nitrous acid, however, yield a mixture of cyclobutanol and cyclopropylcarbinol.



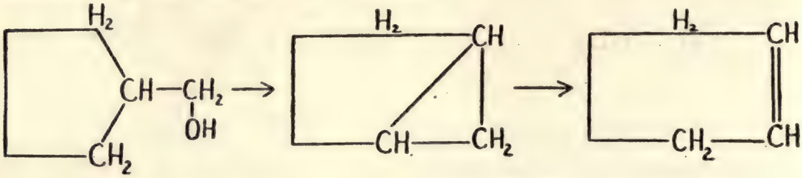
Cyclopentylmethylamine and nitrous acid readily yields cyclohexanol and in the same way cyclohexylmethylamine is converted into cycloheptanol.[4]

Conversion of the cyclopentane ring to the cyclobutane ring has been noted by Rosanov, cyclopentyl nitrite being converted by the action of concentrated alkali into nitromethylcyclobutane.[5]

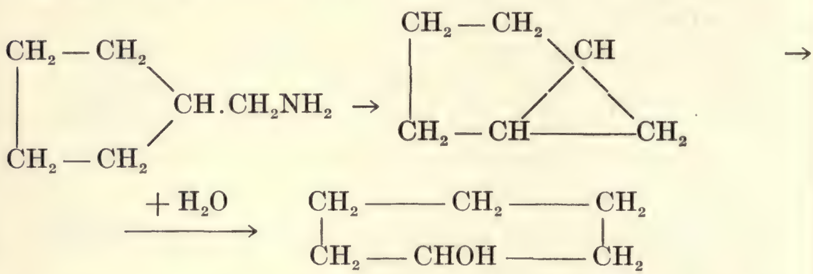


[3] *J. Chem. Soc.* *1910*, I, 838.
[4] Wallach, *Ann.* *353*, 331 (1907).
[5] *J. Chem. Soc. Abs.* *1915*, I, 657.

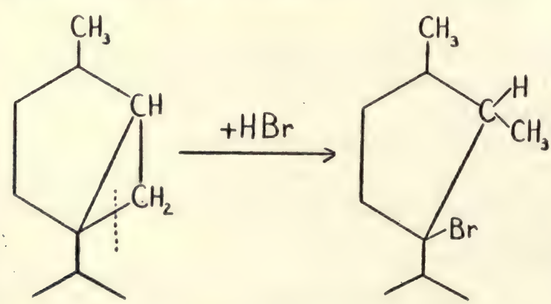
Dehydration of cyclopentylcarbinol by oxalic acid yields cyclohexene, which Rosanov considers is formed with the intermediate formation of the bicylic hydrocarbon,



Probably influenced by his studies of the reactions of sabinene, which contains a three carbon ring, Wallach has offered an explanation of these reactions based upon the intermediate formation of a cyclopropane ring structure as indicated by the following:

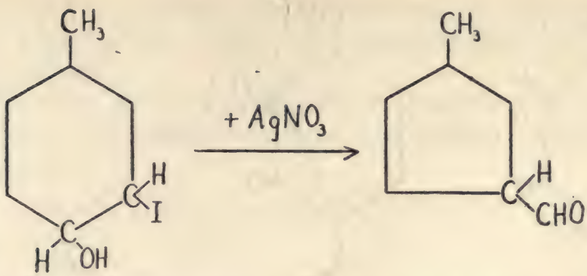


It is curious that when treated with hydrogen bromide, the cyclopropane ring in sabinane is broken in such a way that the five carbon ring, not the six carbon ring, is preserved.[6]



Tiffeneau[7] observed change of the cyclohexane ring to the cyclopentane ring, when 2-iodocyclohexanol is treated with silver nitrate.

[6] Kishner, *J. Russ. Phys.-Chem. Soc.* *43*, 1157 (1911).
[7] *Compt. rend.* *159*, 771 (1914).



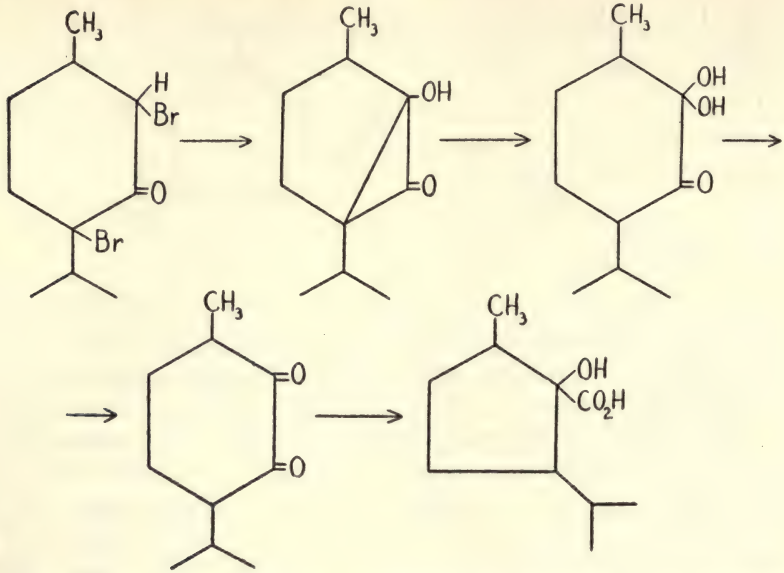
When cyclic α-monochloroketones are treated with alcoholic caustic potash, cyclic acids result in which the number of carbon atoms in the ring is reduced by one.[8] Thus 2-chlorocylohexanone gives cyclopentanecarboxylic acid, and 4-chloro-1-methylcyclohexane-3-one yields methylcyclopentane-3-carboxylic acid. Favorski's experimental work does not show that the carbon atom to which the chlorine is attached is the one which becomes the carboxyl group. Wallach's theory of the intermediate formation of a bicyclic compound is applicable to this case, and explains the function of the alkali which is necessary to effect the change,

$$\begin{array}{l} CH_2 - CH_2 - CHCl \\ | \qquad\qquad\qquad | \\ CH_2 - CH_2 - C = O \end{array} \longrightarrow \begin{array}{l} CH_2 - CH_2 - CH \\ | \qquad\qquad\quad / \; | \\ CH_2 - CH \; - C = O \end{array} + H_2O \longrightarrow$$

$$\begin{array}{l} CH_2 - CH_2 - CH_2 \\ | \qquad\qquad\quad / \\ CH_2 - CH - COOH. \end{array}$$

Wallach has reviewed[9] the rearrangement of dibromocyclic ketones, particularly cyclohexanones, by alkali to hydroxy acids of one less number of carbon atoms in the ring. As a rule the two halogen atoms are substituted not on the same carbon atom as $>CBr_2$ but each halogen replaces a hydrogen atom of the two adjacent carbon atoms. Wallach assumes the intermediate formation of a three-carbon ring derivative leading to the formation of an ortho-diketone. Such diketones when isolated appear to have changed to the ketol, like buchu camphor. Both menthone and carvomenthone give dibromides which yield the same cyclopentane carboxylic acid derivative, which Wallach explains as follows,

[8] Favorski & Boshovski, *J. Russ. Phys.-Chem. Soc. 46,* 1097 (1914).
[9] *Ann. 414,* 296 (1918).



In a study of the Wagner rearrangement Ruzicka [10] obtained evidence which strongly supports the theory of the intermediate formation of cyclopropane derivatives in such reärrangements. As regards the intermediate cyclopropane theory versus the theory of dissociation to bivalent carbon Ruzicka finds that rearrangement takes place with tertiary alcohols, such as methyl borneol and methyl fenchyl alcohol, which could not yield bivalent carbon directly by loss of water. The products of dehydration of methylborneol and methylfenchyl alcohol are identical, which fact Ruzicka considers to be in confirmation of the tricyclene or cyclopropane theory.

Meerwein [11] showed that 1-isopropylcyclopentane-1.6-diol is converted by the pinacoline rearrangement to the six carbon ring 2.2-dimethyl cyclohexanone:

$$\begin{array}{l} CH_2 - CH_2 \qquad\qquad\quad CH_3 \\ | \qquad\qquad\quad >C - C< \\ CH_2 - CH_2 \quad\ |\qquad | \quad CH_3 \\ \qquad\qquad\quad OH \ \ OH \end{array} \longrightarrow \begin{array}{l} CH_2 - CH_2 - CO \\ | \qquad\qquad\qquad\ \ | \quad CH_3 \\ CH_2 - CH_2 - C < \\ \qquad\qquad\qquad\qquad\ \ CH_3 \end{array}$$

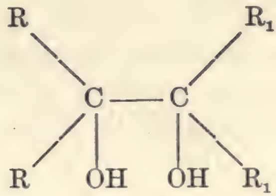
Further work showed that apparently,

(1) By pinacoline rearrangement no intermediate products of the trimethylene or ethylene oxide type could be detected or isolated.

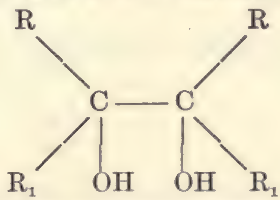
[10] *Helv. Chim. Acta.* I, 110 (1918).
[11] *Ann.* 376, 152 (1910).

(2) The behavior of the cyclic pinacones on rearrangement is essentially a special case of the general rules, holding good also with acyclic pinacones.

(3) The course of the pinacoline rearrangements is determined by different factors according to the structure of the pinacone. In the symmetrical type

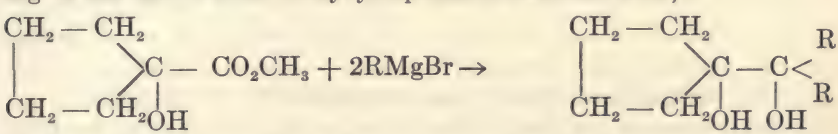


the rearrangement is determined by the ease of "migration" of the groups R and R_1. With those of the unsymmetrical type,

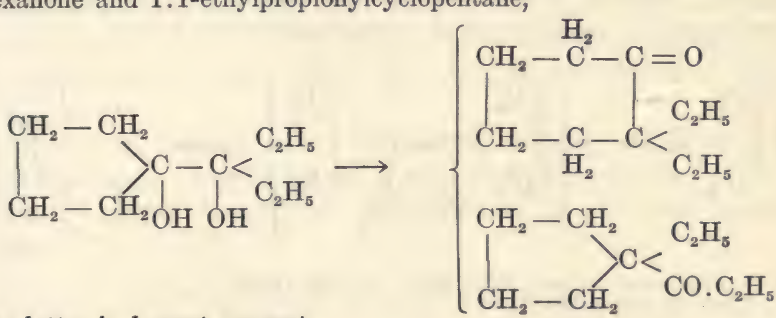


the relative stabilities of the two hydroxyl groups are more important.

Meerwein made the diethyl and diphenyl derivatives corresponding to the above from α-oxycyclopentane carbonic ester,

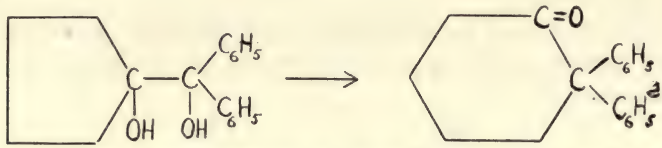


The diethyl derivative yields the two pinacolines, 2.2-diethylcyclohexanone and 1.1-ethylpropionylcyclopentane,

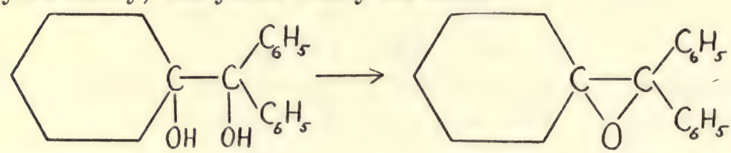


the latter in largest amount.

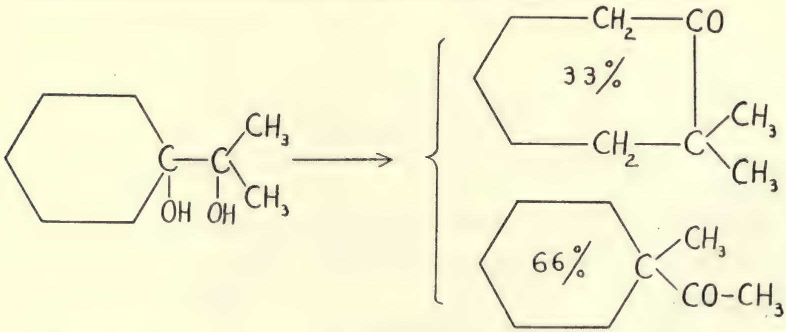
The diphenyl derivative, however, yields the six ring ketone quantitatively,



The *as*-diphenylpentamethylene glycol, however, does not rearrange to the cycloheptanone derivative (as might be expected from Baeyer's theory) but yields chiefly the oxide.

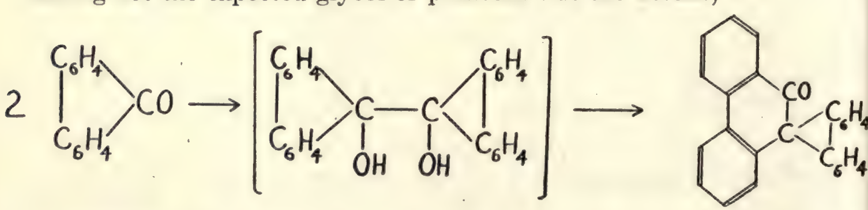


The dimethylpentamethylene glycol gives the two ketones,



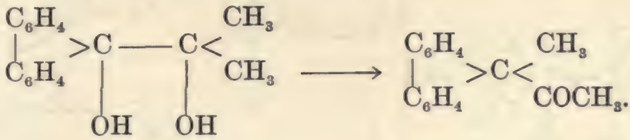
This heptanone derivative was overlooked by Tarbouriech.[12]

Rearrangement of five carbon rings to six carbon rings by pinacoline rearrangement has been observed previously. Klinger and Lonnes [13] reduced fluorenone with zinc dust and acetyl chloride obtaining not the expected glycol or pinacone but the ketone,



[12] *Compt. rend.* *149,* 605, 863 (1909); *150,* 1606 (1910).
[13] *Ber.* *29,* 2154 (1896).

Meerwein shows that the similarly constituted *as*-dimethyl and *as*-diethyldiphenylene glycols yield exclusively the normal pinacoline, without change of the five carbon ring, e. g.,



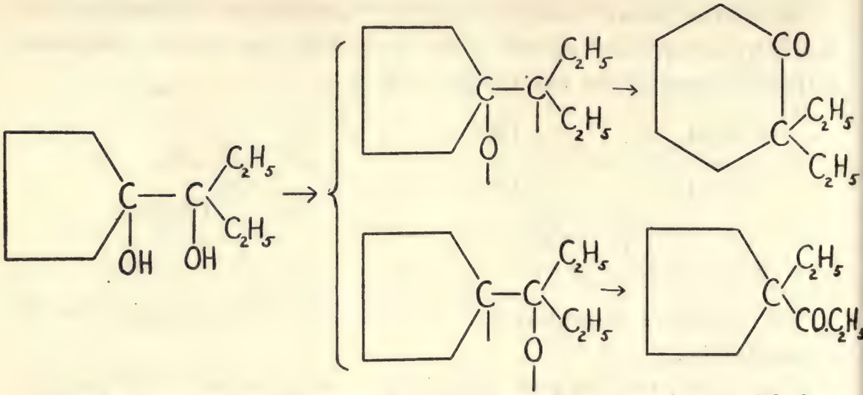
The diphenyl derivative is converted into the six carbon ring of phenanthrene.

The same explanation, pinacoline rearrangement, explains the result noted by Klinger and Lonnes on oxidizing diphenyldiphenylene-ethylene.

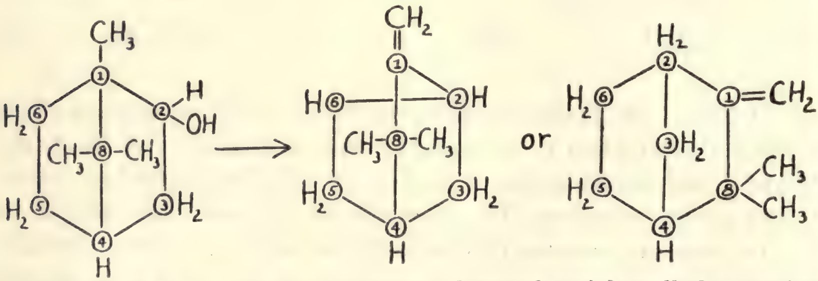
Theory of the Pinacoline Rearrangement: The assumption of intermediate formation of a triatomic ring was made first by Erlenmeyer,[14] who supposed the formation of substituted ethylene oxides. Under special conditions, the formation of ethylene oxide derivatives can be shown in the case of benz-pinacone and *sym.*-diphenylditolylglycol: these particular oxides are converted into ketones on heating with dilute mineral acids. Against the general theory, Meerwein cites the well-known fact that the oxides are usually converted, by addition of water, to glycols under much milder conditions than the latter are converted into pinacones, recalling particularly the case of tetramethylethyleneoxide which takes up water to form the glycol even in the absence of acids. The results of Tiffeneau[15] on the properties of substituted ethylene oxides also support the views of Meerwein.

Meerwein assumes that in diethyltetramethyleneglycol both hydroxyls have approximately equal tendencies to split off as water, therefore, leading to the formation of the two ketones, thus,

[14] *Ber.* *14*, 322 (1881). (Cf. also Nef, *Ann.* *198*, 148 [1879]).
[15] *Ann. chim. phys.* (8) *10*, 346, 375 (1905).



In the conversion of borneol or isoborneol to camphene with loss of water the 1,2,3,4,8 pentamethylene ring is converted into a six carbon ring, and the original six carbon ring, 1 to 6, is converted into a five carbon ring.



Wagner [16] in his original camphene-borneol article called attention to changes of the type,

$$\begin{array}{l} CH_3 \\ CH_3-C-CH-CH_3 \\ CH_3 \qquad\ \ OH \end{array} \longrightarrow \begin{array}{c} CH_3 \qquad\qquad CH_3 \\ >C=C< \\ CH_3 \qquad\qquad CH_3 \end{array}$$

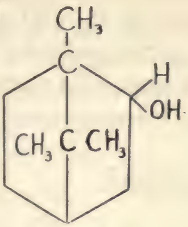
and for which Tiffeneau suggests the name "retropinacoline rearrangement." [17]

For comparison with borneol it is necessary to ascertain the dehydration behavior of,

(1) Alcohols of the cyclohexane series, hydroxyl being in the ring.

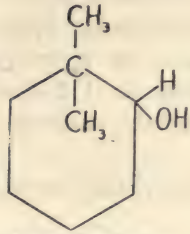
(2) Alcohols of the cyclopentane ring in which the hydroxyl group is in the side chain, for example,

[16] *J. Russ. Phys.-Chem. Soc. 31,* 680 (1899).
[17] *Rev. gen. sci. 18,* 583 (1907).



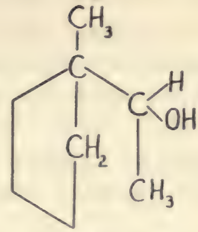
borneol

I



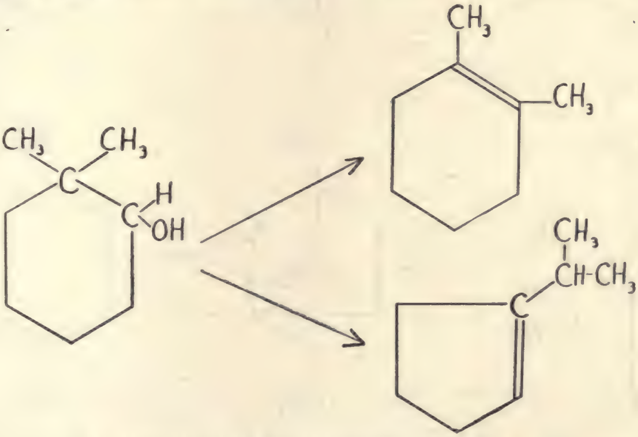
2.2-dimethylcyclohexanol-1

II



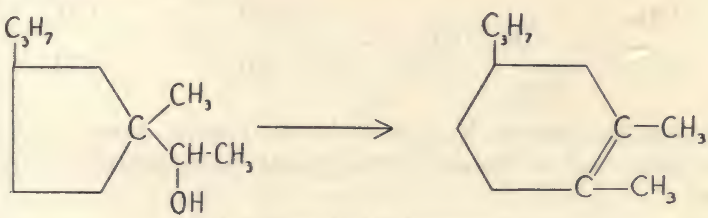
1.1-methyl-α-oxethylcyclopentane

In splitting off water from I, two products result, as indicated,



1.2-dimethyl-Δ¹-cyclohexene — about 75%
Δ¹-isopropylcyclopentene — about 25%

Instead of 1.1-methyl-α-oxethylcyclopentane, Meerwein employed its derivative 3-isopropyl-1.1-methyl-α-oxethylcyclopentane.[18] As in the first instance, the normal product of dehydration was not formed but a mixture as follows:



1.2-dimethyl-4-isopropyl
Δ¹-cyclohexene
principal product

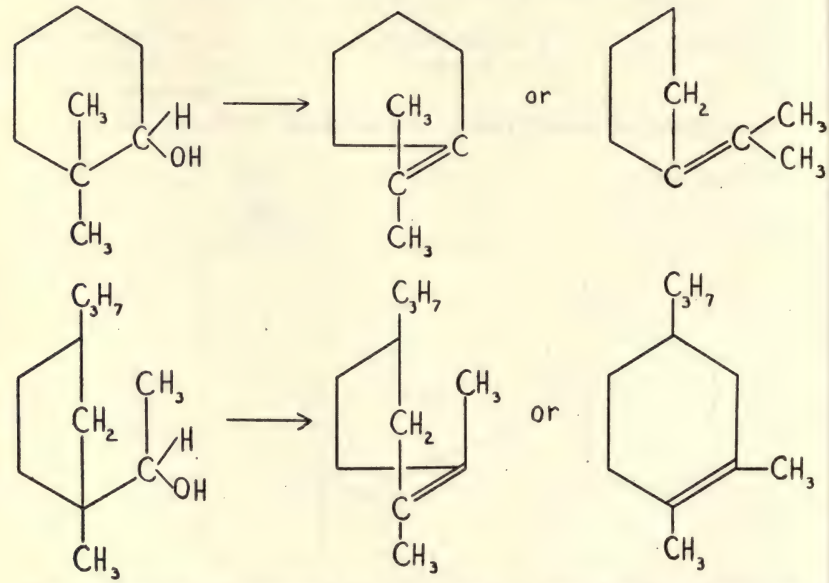
[18] *Ann.* 405, 129 (1914).

The rearrangement of 2.2-dimethylcyclohexanol-1 to Δ^1-isopropylcyclopentene, with decrease in the carbon ring, C_6 to C_5, and also likewise the ring enlargement by rearrangement of 3-isopropyl-1.1-methyl-α-oxethylcyclopentane to 1.2-dimethyl-4-isopropyl-Δ^1-cyclohexene, C_5 to C_6, is completely analogous to the rearrangement of borneol to camphene.

This is made clearer by writing the change as follows:

I

II



The conversion of borneol to camphene is practically a summary of the two reactions above.

Clear explanation will be possible probably only when the *mechanism* of the change of pinacoline alcohol to tetramethylethylene is clear. Zelinsky and Zelikov,[19] like Nef, suppose the formation of a trimethylene ring.

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!\underset{\diagdown\ \ \underset{CH_2}{}\ \ \diagup}{C - CH} - CH_3 \longrightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!C = C\!<\!\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

This explanation has been given for the borneol-camphene change but as pointed out by Semmler [20] the hypothetical intermediate hydrocarbon

[19] *Ber.* *34*, 3251 (1901).

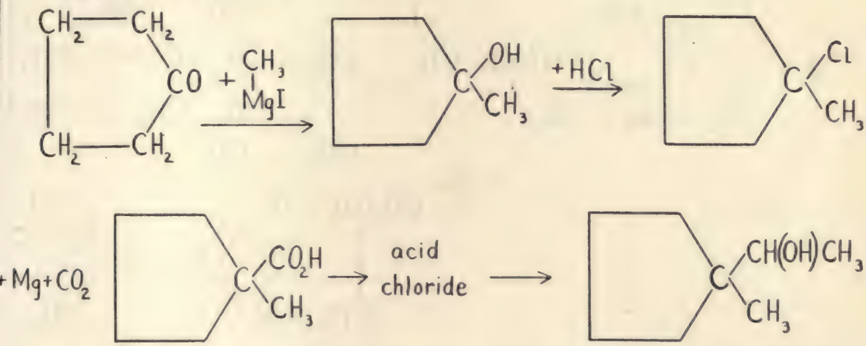
[20] *Ber.* *35*, 1018 (1902); Lipp, *Ber.* *53*, 769 (1920), considers that the reactions of tricyclenic acid support Semmler's constitution for tricyclene.

is completely symmetrical and the resulting camphene should therefore be optically inactive, which generally is not the case.

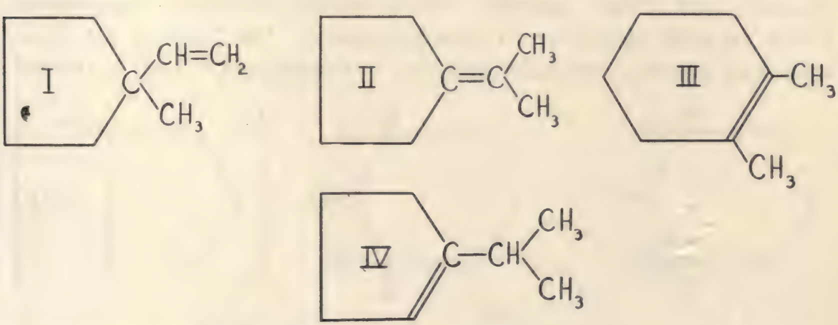
Tiffeneau [21] has suggested that water is split off from pinacoline alcohols as follows:

$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle H\quad OH}{C}-CH_3 \rightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\diagdown\,\diagup}{C}-CH_3 \rightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=C<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$$

Meerwein [22] succeeded in making the desired 1.1-methyloxethyl-cyclopentane as follows:



By warming with $ZnCl_2$ water is readily removed. Of the three possibilities,



II would undoubtedly be rearranged to IV.

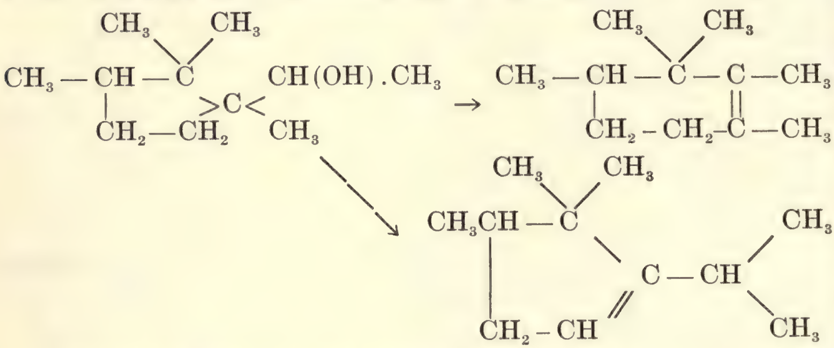
III and IV are known. The substance obtained proved to be very

[21] *Rev. gen. sci.* 18, 583 (1907).
[22] *Ann.* 417, 255 (1918).

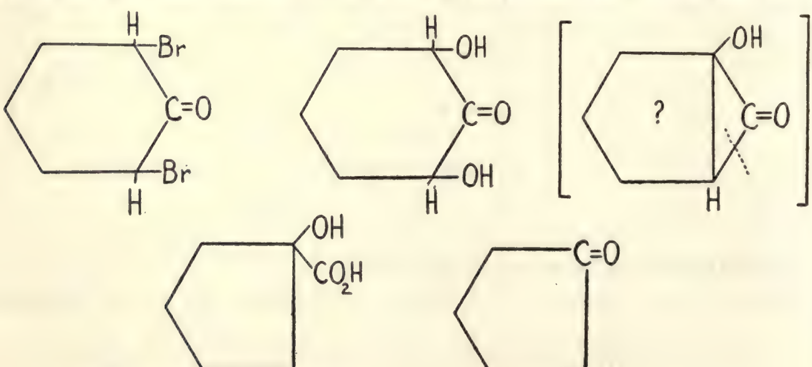
nearly pure 1.2-dimethyl-Δ^1-cyclohexene, or III, boiling-point 135°–137°; $d\frac{20^\circ}{4^\circ}$ 0.8234; $n\frac{20^\circ}{D}$ 1.4566. Oxidation gave 2,7-diketooctane,

$$\begin{array}{l} CH_2 — CH_2 — COCH_3 \\ | \\ CH_2 — CH_2 — COCH_3 \end{array}$$

Meerwein has obtained additional results, parallel to those previously noted, in the case of 1,2,2,3-tetramethyl-1.α-oxethylcyclopentane, which gives, partly with ring enlargement and partly with a rearrangement of a methyl group, 1,2,3,3,4-pentamethyl-Δ^1-cyclohexene and 1,2,2-trimethyl-3-isopropyl-Δ^3-cyclopentene.

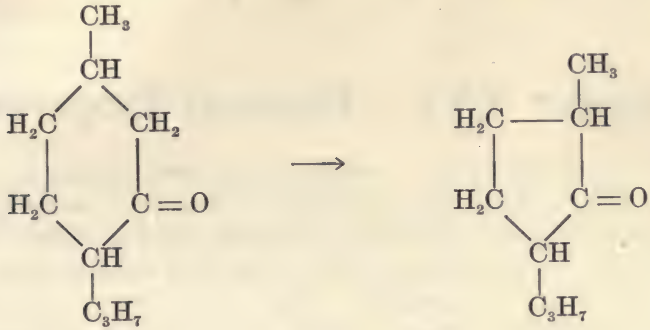


Wallach has described the conversion of a series of cyclohexanone derivatives into cyclopentanones.[23] When cyclohexanone is brominated in acetic acid 1,3-dibromohexane-2-one is formed, which, on treating with dilute aqueous caustic potash at room temperature, yields an acid derivative of cyclopentanone. On treating the latter with lead peroxide and sulphuric acid cyclopentanone itself is formed.



[23] *J. Chem. Soc. Abs. 1916*, I, 487.

Similar reactions were carried out with methylcyclohexanones and in the case of menthone, 1-methyl-3-isopropylcyclopentane-2-one was formed.



Chapter XVI. Physical Properties

With the exception of a comparatively small number of hydrocarbons of the terpene series, the physical properties recorded in the literature of the non-benzenoid hydrocarbons differ so widely in each case that it is very difficult to draw any general conclusions of value from data at present available. Simple derivatives of the hydrocarbons are frequently known in much purer condition and the physical properties determined with much greater accuracy than in the case of the parent hydrocarbons themselves. The tables of physical properties of the simpler paraffine hydrocarbons shown in the accompanying tables show the wide disagreement in physical constants of these simple hydrocarbons. The figure given in the literature for the melting-point of normal octane is —98.2° but recent determinations by Forcrand[1] show that the melting-point of normal octane is —57.4°. Very few of the unsaturated hydrocarbons derived from paraffine hydrocarbons are known in a state of purity and the constitution of many of them are still in doubt. Most of the individuals of this series described thus far are very evidently mixtures of two or more hydrocarbons.

Density and Molecular Volume: The density of individual hydrocarbons is frequently given at temperatures other than zero degrees, 4°, 15°, 17½° or 20° and it is frequently desirable to recalculate the density from the temperature stated to some standard temperature, usually zero or 20°, for the purpose of comparison. Walden has shown that the increase in molecular volume V_M for each degree Centigrade is about 0.11 per cent[2] the molecular volume V_M being equal to the molecular weight divided by the density.

The molecular volumes of the normal paraffines at 0° show an average increment for CH_2 of 15.9.[3]

[1] *Compt. rend.* *172*, 31 (1921).
[2] *Z. physik. Chem.* *65*, 158 (1909).
[3] Kauffmann, Beziehungen zwischen physikalische Eigenschaften u. chemische Constitution, 1920, p. 60.

Hydrocarbon	$V\frac{0°}{M}$	Δ
Pentane	111.8	
		15.4
Hexane	127.2	
		15.8
Heptane	143.0	
		15.9
Octane	158.9	
		16.0
Nonane	174.9	
		15.9
Decane	190.8	
		16.0
Undecane	206.8	
		15.6
Dodecane[4]	222.4	
		16.5
Tridecane	238.9	
		15.8
Tetradecane[4]	254.7	
		16.5
Pentadecane	271.2	
		16.0
Hexadecane	287.2	

The molecular volumes of isomeric hydrocarbons show slight differences, for example,

		$V\frac{20°}{M}$
C_5H_{12}	n.pentane[5]	115.2
"	isopentane[5]	116.4
C_6H_{14}	n.hexane[6]	130.5
"	2-methylpentane[7]	131.1
"	2.2-dimethylbutane[7]	132.8
"	2.3-dimethylbutane[7]	130.2
"	3-methylpentane[8]	129.1

The octanes show only very slight differences in molecular volume, the maximum being that of 2.5-dimethylhexane and the minimum that of 3.4-dimethylhexane,[9]

	$V\frac{15°}{M}$
maximum	163.5
minimum	157.2
n.octane	161.7

The monochlorohexanes also show only slight differences for $V\frac{20°}{M}$

[4] Apparently the observed specific gravities of these two hydrocarbons at 0° are too low by about 0.0009.
[5] Timmermans, *Chem. Zentr. 1912* (2), 472.
[6] Auwers & Eisenlohr, *Z. physik. Chem. 83*, 431 (1913).
[7] Kishner, *J. Russ. Phys.-Chem. Soc. 43*, 595 (1911); *47*, 1111 (1915).
[8] Kishner, *J. Russ. Phys.-Chem. Soc. 45*, 973 (1913).
[9] Clarke, *J. Am. Chem. Soc. 33*, 520 (1911); *34*, 170, 674 (1912).

Maximum, 2-chloro-2-methylpentane	139.7
Minimum, 3-chloro-3-methylpentane,	136.4
n.hexyl chloride	137.7

The molecular volumes and densities of the hydrocarbons of the ethane and propane series have been determined by Maas and Wright.[10]

Hydrocarbon	*B.-P. °C*	d_B	V_M *Experimental*	V'_M *Calcul.*	*Difference* $V_M - V'_M$	$\frac{\Delta V}{\Delta T}$
Ethane	—88.3	0.5459	54.95	55	..	.0044
Propane	—44.5	0.5853	75.2	77	—1.8	.0033
Ethylene	—103.9	0.5699	49.1	44	+5.1	.0045
Propylene	—47.0	0.6095	68.9	66	+2.9	.0034
Acetylene	—83.6	0.6208	41.9	33	+8.9	.0046
Allylene	—27.5	0.6785	59.0	55	+4.0	.0027

d_B densities at the boiling-points.

V_M molecular volumes calculated from d_B

V'_M molecular volumes calculated on the basis $C = 2H = 11$.

$\frac{\Delta V}{\Delta T}$ = the tempertaure coefficients of the specific volume at the boiling-point. The values $\frac{\Delta V}{\Delta T}$ are dependent upon the critical temperatures of the hydrocarbons, which fact makes it possible to calculate the specific volumes of any of the hydrocarbons at any temperature, provided the specific volume at any one temperature is known and the specific volumes for one of the other hydrocarbons is known at all temperatures. This was one of the deductions made by van der Waals from his equation of corresponding states, namely that

$$\frac{V_1 - V_2}{V_2} = \frac{v_1 - v_2}{v_2}$$

where V_1 and V_2 are the specific volumes of one liquid and v_1 and v_2 are the specific volumes of another liquid where V_1 v_1 and V_2 v_2 are measured at the same corresponding temperatures. Taking propylene as a standard Maas and Wright calculated the specific volumes of ethane, ethylene, acetylene, propane and allylene at a temperature 30° higher. The greatest observed discrepancy between the calculated and experimental values was only 0.3%, in the case of propane, the other cases being within the experimental error of 0.1%.

[10] *J. Am. Chem. Soc.* 43, 1105 (1921).

Ring closing usually has a greater effect on the molecular volume than a double bond or branched chain structure, as compared with normal carbon chain structures.

		$V\frac{20^\circ}{M}$
C_6H_{14},	n.hexane	130.5
C_6H_{12},	α-hexene[11]	126.0
"	β-hexene	123.3
"	cyclohexane	108.1
$C_6H_{12}O$,	propylallyl ether	125.1
"	δ-hexylene oxide $CH_2—CH_2—CH—CH_3$ $\mid \qquad\qquad \mid$ $CH_2—CH_2—O$	114.6
$C_6H_{10}O$,	allyl ether	119.3
"	cyclohexanone	101.9
$C_5H_{10}O$,	methylbutyl ether	118.4
"	pentamethylene oxide	97.4

Cyclohexane is thus seen to have a greater density than n.hexene but the true effect of ring closing on the molecular volume is realized by correcting for the volume of the two hydrogen atoms difference between C_6H_{14} and C_6H_{12}. When the value 32.05 for these two hydrogen atoms is substracted from the molecular volume of hexane, $130.5 - 32.05 = 98.4$, the result is lower than the observed value of cyclohexane by 9.7 units. The molecular volume of the saturated cyclic hydrocarbons may be calculated in another manner, i. e., by multiplying the value for CH_2 at 20°, $V\frac{20^\circ}{M} = 16.27$, by the number of such groups in the hydrocarbon. The results show that in all cases the molecular volume of the cyclic hydrocarbons is materially *greater* than the values corresponding to the number of CH_2 groups present. The latter method is designated as II and the former, deducting 32.05 from the $V\frac{20^\circ}{M}$ of the normal hydrocarbons, is method I in the following table.

HYDROCARBON[12]	$V\frac{20^\circ}{M}$ (obs.)	Excess of observed over calculated values	
		I	*II*
Cyclobutane, C_4H_8	81.7		16.6
Cyclopentane, C_5H_{10}	94.1	10.9	12.7
Ccyclohexane, C_6H_{12}	108.1	9.7	10.5
Cycloheptane, C_7H_{14}	121.1	6.6	7.2
Cyclooctane, C_8H_{16}	133.7	3.1	3.5
Cyclononane, C_9H_{18}	163.9	17.4	17.5

[11] v. Braun, *Ann.* *382*, 22 (1911).
[12] Cf. values given by Willstätter, *Ber.* *40*, 3988 (1907); *41*, 1483 (1908); *43*, 1182 (1910).

It might have been expected from Baeyer's strain theory that the closest agreement between the calculated and observed molecular volumes would be in the case of cyclopentane and cyclohexane, instead of cyclooctane. The same order of differences are observed in the case of the ethyl derivatives.

Hydrocarbon	$V\frac{20°}{M}$	*Effect of ring closing; excess of observed over calc.* $V\frac{20°}{M}$
Ethyl cyclopropane[13]	103.3	20.2
Ethyl cyclobutane[14]	115.5	17.1
Ethyl cyclohexane[15]	143.1	12.5
Ethyl cycloheptane[16]	154.8	8.2

The ketone derivatives show the same order of differences, the molecular volume at 20° having a maximum difference from the calculated value in the case of cyclobutanone, minimum in the case of cyclooctanone and again a large difference in the case of cyclononanone.

The effect of ring closing in the case of 3.3-dimethylbicyclohexane,[17] considered as derived from *gem.*dimethylhexane is indicated by a difference of 26.9 units, $V\frac{20°}{M}$ 138.3.

T. W. Richards regards the *relations between boiling-point and density* as a natural corollary of the theory of atomic compressibility or deformability. "Thus, as regards two substances otherwise similar, the less volatile one would be less compressible, denser and possess greater surface tension. These outcomes of the theory correspond with the facts in a majority of cases thus far studied; for example, o-xylene is denser, less volatile, less compressible and possesses a greater surface tension than either m-xylene or p-xylene." [18]

Tyrer has re-examined Trouton's rule and states that the relation between the molecular volume and boiling-point may be better expressed by a modification of Trouton's rule, which Tyrer [19] formulates as follows,

[13] Zelinsky, *Ber.* *46,* 170 (1913).
[14] Kishner, *J. Russ. Phys.-Chem. Soc.* *45,* 973 (1913).
[15] Lebedew, *J. Russ. Phys.-Chem. Soc.* *43,* 1124 (1911).
[16] Markownikow, *Ann.* *327,* 73 (1903).
[17] Zelinsky, *Ber.* *46,* 1466 (1913). In his monograph, Kauffmann makes use of Zelinsky's supposed spirocyclane, which Philipow, *J. prakt. Chem.* *93,* 162 (1916), has shown to be a mixture of methylcyclobutene and methenecyclobutane; Kauffmann's inferences are accordingly incorrect.
[18] *J. Chem. Soc.* *99,* 1211 (1911).
[19] *Phil. Mag.* (6) *20,* 522 (1910).

$$T = K \sqrt[3]{V_M}$$

in which the constant K is 68 for the aliphatic hydrocarbons and ethers, 70 for alkyl chlorides and amines, 74 for the fatty acid esters and bromides and 79 for aliphatic iodides and aromatic hydrocarbons. Like most such rules the constant is subject to considerable variation, for example,

Substance	*T*	V_M	*K*
Methyl bromide	286.	58.2	73.8
Ethyl bromide	312.7	77.7	73.0
Propyl bromide	344.	97.2	74.8
Isopropyl bromide	333.	97.2	71.9
Ethyl chloride	285.2	71.2	68.8
Propyl chloride	319.2	91.4	70.9
Isopropyl chloride	309.5	93.6	68.2
Chloroform	334.1	84.5	76.1
Carbon tetrachloride	349.7	103.7	74.3

Melting-Point.

Ring closing has a much more pronounced effect upon the melting-point. Langmuir comments upon the fact that the physical properties of nitrous oxide are practically identical with those of carbon dioxide at a temperature 3° lower, but that the freezing points of these two substances are in marked contrast to the general agreement, being —102° for nitrous oxide and —56° for carbon dioxide. He states that "This fact may be taken as an indication that the freezing-point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of carbon dioxide is more symmetrical, and has a slightly weaker external field of force than that of nitrous oxide." Organic chemists, however, in studying the relations between structure and physical properties, have paid much greater attention to boiling-points, specific gravities and optical properties. Probably on account of the fact that, as Langmuir points out, the freezing-point is so sensitive to differences in molecular structure, it is very difficult to trace simple relationships or make any useful generalizations. Also, since most of the non-benzenoid hydrocarbons and their simple derivatives, of which we have fairly complete knowledge, are oils at ordinary temperatures, data as to their freezing-points are usually lacking.

Most of the non-benzenoid hydrocarbons which are solid at ordinary temperatures are normal paraffines, and of these none of their many possible isomers are known, so that no data exist from which

to draw any conclusions as to the effect of variations in structure upon the melting-point.

The melting-points of the normal paraffines are given in the following table, in which it will be noticed that the increment for CH_2 is irregular in the lower part of the series but becomes more regular and smaller with increase in molecular weight. The melting-point of n.heptane given is probably too low.

Hydrocarbon[20]	*Melting-Point* °C	*Boiling-Point* °C
CH_4	−184.	−164.
C_2H_6	−172.	−84.1
C_3H_8	−189.	−44.5
C_4H_{10}	−135.	−0.1
C_5H_{12}	−130.8	+36.2
C_6H_{14}	−94.3	68.9
C_7H_{16}	−97.1	98.4
C_8H_{18}	−57.4	125.8
C_9H_{20}	−51.	149.5
$C_{10}H_{22}$	−32.	173.
$C_{11}H_{24}$	−26.5	194.5
$C_{12}H_{26}$	−12.	214.5
$C_{13}H_{28}$	−6.2	234.
$C_{14}H_{30}$	+5.5	252.5
$C_{15}H_{32}$	10.	270.5
$C_{16}H_{34}$	18.	287.5
$C_{17}H_{36}$	22.5	303.
$C_{18}H_{38}$	28.	317.
$C_{19}H_{40}$	32.	330.
$C_{20}H_{42}$	36.7	
$C_{21}H_{44}$	40.4	
$C_{22}H_{46}$	44.4	
$C_{23}H_{48}$	47.7	
$C_{24}H_{50}$	51.1	
$C_{31}H_{64}$	68.1	
$C_{32}H_{66}$	70.5	

According to Tsakalotos[21] the curve connecting the melting-points of the normal paraffines is fairly regular and smooth from about $C_{16}H_{34}$ and upwards in the series, and agree well with the values calculated from the formula $\Delta n = \frac{85-0.01882(n-1)^2}{n-1}$ where Δn is the difference between the melting-point of one member and the next highest in the series and n is the number of carbon atoms in the molecule of the hydrocarbon the lower in the series (of the pair).

[20] Methane, Moissan & Chavanne, *Compt. rend.* *140,* 409 (1905); ethane, Ladenburg, *Ber.* *33,* 638 (1900); propane, Maas & Wright, *J. Am. Chem. Soc.* *43,* 1100 (1921); C_4H_{10} to C_8H_{18}, Timmermans, *Chem. Zentr.* *1911* (2), 1015; C_9H_{20} *et. seq.* Krafft, *Ber.* *15* 1687 (1882); *19,* 2218 (1886); *21,* 2256 (1888).

[21] *Compt. rend.* *143,* 1235 (1906); Forcrand [*Compt. rend.* *172,* 31 (1921)] states that the simpler normal paraffines, and the cyclic hydrocarbons C_3 to C_8 follow the rule of the alternance of melting-points.

The substitution of chlorine causes marked rise in the melting-point.[22]

Substance	*Melting-Point* °C	*Boiling-Point* °C
CH_4	−184.	−164.
CH_3Cl	−103.6	−23.4
CH_2Cl_2	−96.7	+41.6
$CHCl_3$	−63.3	61.2
CCl_4	−22.95	76.7
CH_3CH_3	−172.1	−84.1
CH_3CH_2Cl	−138.7	+12.5
CH_3CHCl_2	−96.7	+57.3
$CH_2Cl.CH.Cl_2$	−35.5	...
$CHCl_2.CCl_3$	−29.0	+161.9
$CCl_3.CCl_3$	+187.	+189.6

Unsaturation usually causes a marked rise in melting-point,[23] in the case of hydrocarbons.

Ethane	−172.1	Propane	−189.9
Ethylene	−169.4	Propylene	−185.2
Acetylene	−81.8	Allylene	−104.7

It is of interest to note the very great differences in the melting-points of the following pairs of isomers, noting that the differences in boiling-point are by no means so large.

	Melting-Point	*Boiling-Point*
n.pentane, $CH_3(CH_2)_3CH_3$[24]	−130.8°	+36.2°
tetramethylmethane, $(CH_3)_4C$.	−20. °	+9.5°
n.octane, $CH_3(CH_2)_6CH_3$[25]	−57.4°	125.8°
2.2.3.3.tetramethylbutane[26] $(CH_3)_3C.C(CH_3)_3$	+103.°–104.°	106.°–107.°

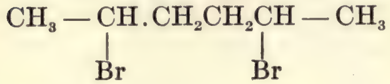
The effect of ring closing upon the melting-point is to raise it and, as will be noticed above, the boiling-point is also raised.

	Melting-Point		*Melting-Point*
n.hexane	−93.5°	n.octane	−98.2°
cyclohexane	+6.4°	cyclooctane	+11.5°

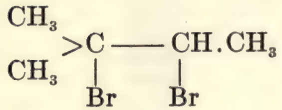
[22] Timmermans, *loc. cit.*
[23] Maas & Wright, *J. Am. Chem. Soc. 43,* 1100 (1921).
[24] Timmermans, *Chem. Zentr. 1911* (2), 1015.
[25] Forcrand, *Compt. rend. 172,* 31 (1921).

[26] The similarly constituted undecane, $(CH_3)_3C - \overset{CH_3}{\underset{CH_3}{C}} - C)CH_3)_3$, and tetradecane, $(CH_3)_3C - \overset{CH_3}{\underset{CH_3}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - C(CH_3)_3$ are not known but, by analogy, their melting-points would be much higher than n.undecane and n.tetradecane.

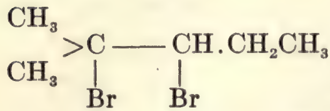
The very marked effect of structural differences on the melting-point is well illustrated by the dibromohexanes. Increase in the number of methyl groups, and proximity of these methyl groups to the bromine or other negative substituent raises the melting-point as compared with isomeric derivatives, for example,



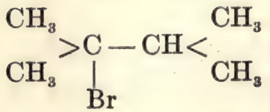
melting-point 38.2°
(n.isomers are liquid)



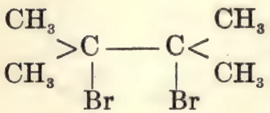
melting-point 7°



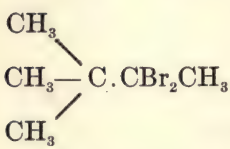
liquid



melting-point 24°–25°

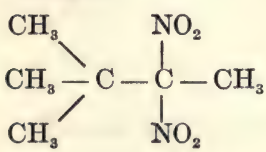


melting-point 169°–170°
corresponding dichloro,
melting-point160°

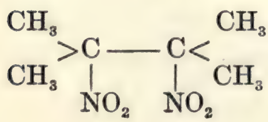


melting-point 187°
corresponding dichloro,
melting-point 151°

Nitro groups similarly placed result in crystalline derivatives, for example,



melting-point 173°–174°



melting-point 213°–214°

The melting-point of the latter substance is higher than that of any of the dinitro or trinitro benzenes. Dinitroheptane and octane of similar structures are also well crystallized substances,

$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>\!\underset{NO_2}{\overset{|}{C}} - CH_2 - \underset{NO_2}{\overset{|}{C}}\!<\!\!\begin{array}{l} CH_3 \\ CH_3 \end{array} \qquad \text{melting-point } 81°\text{–}82°$$

$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>\!\underset{NO_2}{\overset{|}{C}} - CH_2.CH_2 - \underset{NO_2}{\overset{|}{C}}\!<\!\!\begin{array}{l} CH_3 \\ CH_3 \end{array} \qquad \text{melting-point } 124°\text{–}125°$$

Closing of the ring raises the boiling-point slightly, as a comparison of butane and cyclobutane and a number of their derivatives indicates,

n. butane series	*Boiling-Point °C*	*Cyclobutane series*	*Boiling-Point °C*	*Difference °C*
n.butane	—0.1	c.butane	+11.	+11.
C_4H_9Cl	+77.	$C_4H_7.Cl$	85.	+8.
$C_4H_9NH_2$	76.	$C_4H_7.NH_2$	81.	+5.
$C_4H_9.Br$	100.	$C_4H_7.Br$	104.	+4.
$C_4H_9.OH$	116.	$C_4H_7.OH$	122.5	+6.5
C_4H_9I	131.	$C_4H_7.I$	138.	+7.
$C_4H_9.CO_2H$	186.	$C_4H_7.CO_2H$.	195.	+9.

When the two series of hydrocarbons of three to eight carbon atoms are compared, the cyclic series is seen to have consistently higher boiling-points.

Boiling-points of cyclic and normal hydrocarbons.

Normal	*Boiling-Point °C*	*Cyclic*	*Boiling-Point °C*	*Difference °C*
Propane	—44.5	Cyclopropane	—35.	+ 9.5
Butane	—0.1	Cyclobutane	+11.	+10.5
Pentane	36.2	Cyclopentane	49.	+12.8
Hexane	68.9	Cyclohexane	81.	+12.1
Heptane[27]	98.8	Cycloheptane	117.2±.2	
Octane	125.8	Cyclo-octane	145. ±.2	+19.4

Among observations of the boiling-point a few qualitative generalizations can be made, for example, Wallach[28] has noted that in a series of isomeric ketones the widest separation of the ketone group and the alkyl side chain gives the highest boiling-point.

[27] Forcrand, *Compt. rend.* *172*, 31 (1921).
[28] *Ann.* *397*, 183 (1913).

The effect of unsaturation on the boiling-point and critical temperature in the ethane and propane series has recently been shown by Maas and Wright.[29] The figures given in the fourth column show that the boiling-points are approximately equal fractions of the critical temperatures, when figured as degrees absolute.

Hydrocarbons	*Boiling-Point °C*	t C°	*Mol. Latent Heat Evaporation*	*Boiling-Point* / t C.
Ethane	—88.3	35.0	3800	0.60
Ethylene	—103.9	9.9	3510	0.60
Acetylene	—83.6	36.5	5150	0.61
Propane	—44.5	95.6	4500	0.62
Propylene	—47.0	92.1	4600	0.62
Allylene	—27.5	127.9	5230	0.61

The critical values of a number of hydrocarbons of the methane series are given by Young.[33]

Hydrocarbon	*Crit. Pressure mm. Hg.*	*Crit. Temp. °C*	*Crit. Density*	*Density at 0°/4°*
n. Pentane	25100	197.2	0.2323	0.64536
Isopentane	25018	187.8	0.2343	0.63927
n. Hexane	22510	234.8	0.2344	0.67703
Diisopropyl	23360	227.3	0.2411	0.67948
n. Heptane	20430	266.8	0.2341	0.70048
n. Octane	18730	296.2	0.2327	0.71854
Diisobutyl	18660	276.8	0.2366	0.71021
Cyclohexane	30278	280.	0.2735	0.79675
Benzene	36395	288.5	0.3045	0.90006

Absorption of Light; Color: All saturated hydrocarbons are colorless but show selective absorption in the infra red.[30] Examination of hexane, cyclohexane and camphane shows no well defined absorption band in the ultraviolet part of the spectrum, of wave lengths greater than 185 μμ, but ring formation seems to cause a shift of general absorption toward the longer waves. Certain recent works[31] state that unsaturated hydrocarbons show no selective absorption in the ultraviolet but, on the contrary, ethylenic hydrocarbons show definite absorption bands and, in the case of the doubly conjugated fulvenes, absorption bands occur in the visible part of the spectrum, these hydrocarbons being colored yellow to orange. The aliphatic olefines isobutylene, trimethylethylene, hexylene and octylene show two absorption bands, at λ230–λ205 and at about λ180.[32] The presence of

[29] *Loc. cit.*
[33] *Sci. Proc. Roy. Soc. Dublin 12,* 374 (1910).
[30] Coblentz, *Jahrb. Radioakt. 4,* 7 (1908).
[31] Watson, Color in Relation to Chemical Composition, 1918, p. 66.
[32] Stark, Steubing, Enklaar & Lipp, *J. Chem. Soc. Abs. 1913,* II, 363.

two double bonds, not in conjugated positions, causes an intensification of the two absorption bands observed in the case of the singly unsaturated hydrocarbons, as in diallyl and geraniolene. Two conjugated double bonds as in isoprene, 2-3-dimethylbutadiene, and hexadiene-(1.4) show a shift in the position of the two bands of about 20 to 30 μμ, toward the visible spectrum, and an intensification of both bands.

Camphene and α-pinene show an absorption band at λ204–λ198. In limonene and sylvestrene the head of the absorption band is about λ185 but in the case of α and β-phellandrene two bands are clearly developed.

Fulvene is a yellow oil and dimethylfulvene,

$$\begin{array}{l} CH = CH \\ | \\ CH = CH \end{array} \!\!>C=C<\!\! \begin{array}{l} CH_3 \\ \\ CH_3 \end{array}$$

shows three well developed absorption bands with heads at λ370, λ258 and λ207 respectively.

A hydrocarbon of the empirical formula $C_{15}H_{22}$ and containing four double bonds has been described by Sherndall[34] as having an intense *blue* color and accordingly named azulene. The hydrocarbon combines with eight atoms of hydrogen, in the presence of colloidal palladium, forming $C_{15}H_{26}$. The hydrocarbon is probably a tricyclic sesquiterpene perhaps identical with α-gurjunene. It readily combines with picric acid, forming black needles melting at 118°. The intensity of the color is indicated by the fact that 0.064 g. of azulene in 1 liter of gasoline is matched in color by an ammoniacal copper sulfate solution containing 0.24 g. copper sulfate per liter. The very exceptional color of azulene as compared with the fulvenes, renders the confirmation of Sherndall's work, and particularly the purity of the material employed, very desirable.

The absorption spectra of cyclohexene and cyclohexadiene are of interest on account of the fact that they are very different from the absorption spectrum of benzene. The first two hydrocarbons show broad bands differing greatly from the groups of narrow bands of benzene and naphthalene.[35]

Fluorescence: No non-benzenoid hydrocarbons are known which exhibit fluorescence. The marked fluorescence of petroleum distillates is undoubtedly due to traces of substances of the nature of chrysene,

[34] *J. Am. Chem. Soc.* *37*, 1537 (1915).
[35] Stark & Levy, *Jahrb. Radioakt.* *10*, 179 (1913) ; *J. Chem. Soc. Abs.* *1913*, II, 366.

fluorene or pyrene, although the substances which cause fluorescence in these oils have never been isolated and identified. They are easily sulfonated and are, therefore, removed to a large extent on refining such oils with concentrated sulfuric acid, appearing as water-soluble sulfonic acids. It has been suggested by Schulz [36] and others that the blue fluorescence of petroleum distillates is due to colloidally dispersed particles of carbon, sulfur or other material but oils which are carefully dried and filtered are optically homogenous under the ultramicroscope and the fluorescence is in no way affected by an electrostatic field.[37] The formation of such fluorescent material is almost universally observed when organic material is partially carbonized by heat, even in the heating or "boiling" of linseed oil. The manner in which "deblooming" agents, such as nitrobenzene or nitronaphthalene, suppress this property is not known but it is probably a purely physical phenomenon.[38] Ether, benzene and amyl alcohol intensify the fluorescence and aniline and carbon bisulfide suppress it, changing the blue fluorescence of petroleum oils to a dull faint green.

Refractivity: Refractivity has been frequently employed as an aid in determining the constitution of organic compounds and the constants of a great many substances have been studied and correlated. Although the refractive indices of most organic substances fall within the range 1.30 to 1.70, most instruments of reputable make are accurate to the fourth decimal place and only a few drops of liquid substance are required for the determination. However, in order that the molecular refractivity may be calculated, it is necessary to know the density. It is assumed that most of the readers of this volume are familiar with the refractometer and it will suffice to recall the two formulæ for molecular refractivity which are in common use, the n^2 formula proposed by H. A. Lorentz and L. Lorenz [39] in 1880 being the one most frequently employed.

(1) Derived from Gladstone and Dale $\quad M = \frac{n-1}{d} m.$

(2) Lorenz and Lorentz, $\quad M = \frac{n^2-1}{n^2+2} \cdot \frac{m}{d}.$

The Lorenz and Lorentz formula is practically independent of tem-

[36] Petroleum, 5, 205.
[37] Brooks & Bacon, *J. Ind. & Eng. Chem.* 6, 623 (1914).
[38] Kauffmann, *Ann.* 393, 1 (1912).
[39] *Wied. Annalen.* 9, 641; *11,* 70 (1880).

perature and pressure. When the refractive index is accurately determined to the fourth decimal place, the molecular refraction of substances having molecular weights of about 100 will be accurate within ± 0.2. Gladstone and Dale[40] discovered that the refractivity of organic substances is modified by the manner of combination of their constituent atoms; in other words, refractivity is a constitutive property. The study of refractivity with reference to chemical constitution has been developed particularly by Brühl and Auwers. Although the values for the group CH_2, obtained by Brühl and Conradi and Landolt, agree fairly close, Eisenlohr[41] has recalculated this value from data of 503 carefully purified substances, with the results shown in the following, for the sodium D line.

	Number of Substances	Na_D
Hydrocarbons	66	4.624
Aldehydes and ketones	92	4.626
Acids	74	4.613
Alcohols	81	4.634
Esters	190	4.605
	mean	4.618

The values obtained by Conradi[42] and by Eisenlohr are as follows:

Element	Na_D *(Conradi)*	Na_D *(Eisenlohr)*
Carbon	2.50	2.418
CH_2	4.60	4.618
H	1.05	1.100
O, as in $>C=O$	2.28	2.211
O, as in ethers	1.68	1.643
O, as in $-OH$	1.52	1.525
Cl	5.99	5.967
Br	8.92	8.865
I	14.12	13.900
Ethylene bond $>C=C<$, increment		1.733
Acetylene bond $-C\equiv C-$, increment		2.398

The exaltation caused by an ethylene bond was computed from observations on the following hydrocarbons,

[40] *Phil. Trans. 153,* 323 (1863).
[41] *Z. physik. Chem. 75,* 585 (1910).
[42] *Z. physik. Chem. 3,* 210 (1889).

		Mol. Wt.	*Boiling-Point*	*D*	M_D
Amylene [43]	C_5H_{10}	70.08	34. °–35. °	$0.6476\frac{20°}{4°}$	24.81
Amylene [44]	"	70.08	36.7°	$0.6664\frac{16°}{4°}$	24.83
Hexylene [45]	C_6H_{12}	84.10	68. °–68.5°	$0.6792\frac{23°}{4°}$	29.65
Hexylene [44]	C_6H_{12}	84.10	67. °	$0.6885\frac{15°}{4°}$	29.57
Octylene [44]	C_8H_{16}	112.1	121.8°	$0.7255\frac{16°}{4°}$	38.74
Decylene [44]	$C_{10}H_{20}$	140.2	154. °	$0.7720\frac{17°}{4°}$	47.17

Diallyl, d.limonene and sylvestrene were also used by Eisenlohr.

Eijkman [46] estimates that the exaltation in refractivity of ethylene bonds increases with the number of radicals attached to the doubly linked carbon atoms, as follows,[47]

One radical, $RCH=CH_2$	1.60
Two radicals, $RCH=CHR$	1.75
Three radicals, $R_2C=CHR$	1.88
Four radicals $R_2C=CR_2$	2.00

Le Bas [48] has noted that usually introduction of methyl groups into ring structures produces exaltation,

(1) In trimethylene ring $= 0.39$
(2) In tetramethylene ring $= 0.15$
(3) In cyclopentane and cyclohexane ring $= 0.15$

In cases where two methyl groups are in the 1.1 or 1.2 positions this exaltation disappears.

The values for nitrogen and sulfur also vary according to the manner of their combination.

Nitrogen [49]	Na_D
Hydroxylamines	2.48
Amines, primary	2.45
Amines, secondary	2.65
Amines, tertiary	3.00
Nitrites, aliphatic	3.05
Oximes, aliphatic	3.93
Nitro Group, [50]	
nitroparaffines	6.72
Benzenoid derivatives	7.30

Sulfur [51]	Na_D
Mercaptans	7.69
Sulfides	7.97
Thiocyanates	7.91
Disulfides	8.11

[43] Brühl, *Ann.* *200*, 181 (1880).
[44] Landolt & Jahn, *Z. physik. Chem.* *10*, 302 (1892).
[45] Brühl, *J. prakt. Chem.* (2) *49*, 241 (1894).
[46] *Chem. Weekblad.* *3*, 706 (1906).
[47] This is by no means an infallible rule as cases are known in which substitution of a methyl group causes a decrease in refractivity; for example, styrene and methylstyrene, cf. Auwers & Eisenlohr, *J. prakt. Chem.* (2) *82*, 65 (1910).
[48] *Trans. Faraday Soc.* *13*, 53 (1917).
[49] Brühl, *Z. physik. Chem.* *79*, 1 (1912).
[50] Brühl, *Z. physik. Chem.* *25*, 647 (1898).
[51] Price and Twiss, *J. Chem. Soc.* *101*, 1259 (1912).

Brühl[52] concludes that ring closing does not, of itself, affect the molecular refraction, except in the two types to which attention has already been called, i. e., ethylene and cyclopropane. The agreement between the calculated and observed molecular refractivities in the cyclic series is fairly close.[53]

	M *Observed*	*M* *Calculated*
Cyclobutane	18.22	18.41
Cyclopentane	23.09	23.01
Cyclohexane	27.67	27.62
Cycloheptane[54]	32.18	32.22
Cyclooctane	36.58	36.82
Cyclononane	42.36	41.61

Attention has already been called to the instability, or condition of stress, of cyclopropane. Östling[55] has examined a large number of cyclopropane and cyclobutane derivatives. The following values are typical, and indicate that ring closing in the case of cyclopropane produces an exaltation of approximately 0.70 or a little less than one half that produced by a single ethylene bond.

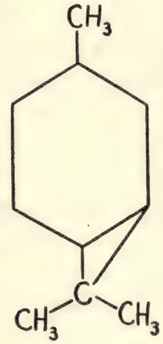
Exaltation of Molecular Refractivity Caused by Ring Closing; Cyclopropanes.

Formula	*Boiling-Point*	$D\frac{t}{4}$	*Exaltation for* M_D
$CH_2{<}\begin{array}{l}CH.CH_3\\ \vert\\ CH.CH_3\end{array}$	32.6°– 33.2°	$0.6755\frac{22°}{4°}$	0.68
$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}{>}C\ CH.CH_3$[56]	37.5°	$0.7052\frac{18°}{4°}$	0.92
$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}{>}CH.CH_2OH$[57]	123.3°	$0.8995\frac{17.5°}{4°}$	0.71
$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}{>}CH.CO_2H$[56]	183.2°–184.°	$1.0897\frac{19°}{4°}$	0.68
$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}{>}CH\ CHO$[57]	98.° (737 mm.)	$0.9294\frac{17°}{4°}$	0.90
$\begin{array}{l}CH_2\\ \vert\\ CH_2\end{array}{>}C{<}\begin{array}{l}CO_2CH_3\\ \\ CO_2CH_3\end{array}$	196.6°	$1.1509\frac{15.7°}{4°}$	0.71
Sabinane	156.2°–156.8°	$0.8142\frac{19°}{4°}$	0.70
Sabinene[58]	163.°–165.°	$0.8422\frac{17°}{4°}$	1.36
Carane[59]	49.°–50.° (9 mm.)	$0.8381\frac{20°}{20°}$	0.93

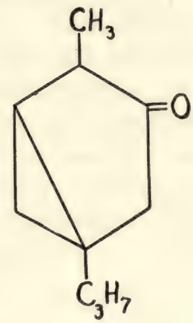
[52] Cf. *Ber.* *25*, 1952 (1892); *27*, 1065 (1897).
[53] Cf. Auwers, *J. Chem. Soc. Abs.* *1918*, II, 343; *Ann.* *422*, 133 (1921).
[54] Willstätter & Kametaka, *Ber.* *41*, 1483 (1908).
[55] *J. Chem. Soc.* *101*, 457 (1912).
[56] Gustavson & Popper, *J. prakt. Chem.* (2) *58*, 458 (1898).
[57] Demjanov & Fortunov, *Ber.* *40*, 4397 (1907).
[58] Auwers, Roth & Eisenlohr, *Ann.* *373*, 275 (1910).
[59] Semmler & Feldstein, *Ber.* *47*, 384 (1914).

The effect of a double bond in a conjugated position to the cyclopropane ring produces increased exaltation, as shown by sabinene, and an aldehyde or ketone group adjacent to the cyclopropane ring also produces a definite, though slight increase in exaltation, as is shown by cyclopropyl formaldehyde, exaltation for $M_D = 0.90$. Of the following three ketones I and II show increased exaltation while III, in which the carbonyl group is not conjugated with reference to the cyclopropane group, shows the average exaltation.

increment
$M_D = 0.89$



increment
$M_D = 1.03$



increment
$M_D = 0.70$ or 0.76

The hydrocarbon 1,2,3, *trimethyl*cyclopropane shows the abnormally large increment for M_D of 1.37 which harmonizes with the observations of Le Bas and Eijkman, noted above, as to the effect of methyl groups. Closing of the ring as in cyclopropane has no effect upon the *molecular dispersion* but the conjugation of a cyclopropane ring and an ethylene bond causes an increase of approximately 10 per cent.

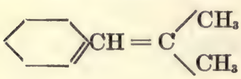
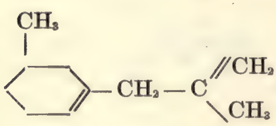
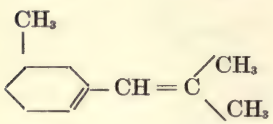
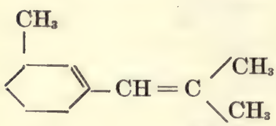
The increment in molecular refractivity produced by the cyclobutane group is smaller and is influenced somewhat by substituent groups, as in the case of cyclopropane derivatives.

Exaltation of Molecular Refractivity Caused by Ring Closing; Cyclobutane Series.

Formula	*Boiling-Point*	$D\frac{t}{4}$	*Increment for* M_D
CH_2-CH_2 [60] $\vert \quad\quad \vert$ CH_2-CH_2	10.°–11.°	$0.703\frac{0^\circ}{4^\circ}$	0.21
CH_2-CH_2 [61] $\vert \quad\quad \vert$ $CH_2-C=O$	98.5°–99.°	$0.9381\frac{16^\circ}{4^\circ}$	0.49
CH_2-CH_2 [62] $\vert \quad\quad \vert$ $CH_2-C\langle^{H}_{OH}$	122.5° [64]	$0.9159\frac{20^\circ}{4^\circ}$	0.42
		$0.9226\frac{15^\circ}{15^\circ}$	0.43
CH_2-CH_2 [63] $\vert \quad\quad \vert$ $CH_2-C\langle^{H}_{CO_2H}$	195.°	$1.0570\frac{16.6^\circ}{4^\circ}$	0.46
CH_2-CH_2 $\vert \quad\quad \vert$ $CH_2-CH.CO_2C_2H_5$	157.°	$0.9525\frac{19.8^\circ}{4^\circ}$	0.43
CH_2-CH_2 $\vert \quad\quad \vert$ $CH_2-C\langle^{CO_2C_2H_5}_{CO_2C_2H_5}$ [63]	104.°–105.° 12 mm.	$1.0456\frac{20^\circ}{4^\circ}$	0.37
$CH_2-CH.CO_2C_2H_5$ [65] $CH_2-CH.CO_2C_2H_5$	114.5° 20 mm.	$1.1191\frac{17.3^\circ}{4^\circ}$	0.54
d.*a* pinene	156.4°–156.6°	$0.8594\frac{18^\circ}{4^\circ}$	0.46
nopinone	118.2° 43 mm.	0.9827	0.57

[60] Willstätter, *Ber.* *40*, 3982 (1907).
[61] Kishner, *J. Russ. Phys.-Chem. Soc.* *37*, 106 (1905).
[62] Brühl, *Ber.* *32*, 1222 (1899).
[63] Zelinsky & Gutt, *Ber.* *40*, 4744 (1907).
[64] Demjanov & Doyarenko, *J. Russ. Phys.-Chem. Soc.* *43*, 835 (1911); *Chem. Abs.* *6*, 478 (1912).
[65] Auwers, *Ann.* *373*, 274 (1910).

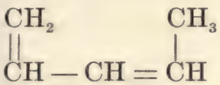
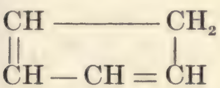
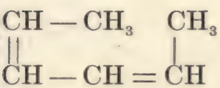
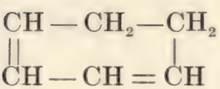
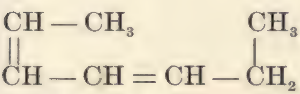
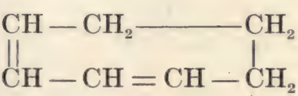
Exaltation of Molecular Refraction Caused by Conjugation of Two Ethylene Linkings.

Substance	M_D Calc.	M_D Obs.	EM_D	Reference
$\Delta^{1,1}$-dicyclohexene, $C_{12}H_{16}/=^2$	52.34	52.65	0.31	66
$\Delta^{3,8(9)}$-p-menthadiene, $C_{10}H_{16}/=^2$.........	45.24	46.0	0.76	67
$\Delta^{2,8(9)}$-m-menthadiene, $C_{10}H_{16}/=^2$	45.24	46.6	1.36	67
$\Delta^{3,8(9)}$-m-menthadiene, $C_{10}H_{16}/=^2$	45.24	46.3	1.06	67
$\Delta^{1,8(9)}$-O-menthadiene, $C_{10}H_{16}/=^2$	45.24	46.0	0.76	68
 $C_{10}H_{16}/=^2$.......	45.24	45.69	0.45	69
 $C_{11}H_{18}/=^2$....	49.86	50.13	0.27	69
 $C_{11}H_{18}/=^2$....	49.86	50.39	0.54	69
 $C_{11}H_{18}/=^2$....	49.86	49.97	0.11	69

In a recent paper Auwers [70] carefully reviews the effect of ring closing on the molecular refraction, particularly in the cyclohexane series on account of the evidence of refractivity as to the constitution of benzene. Although the refractivities of the saturated cyclopentanes, cyclohexanes and cycloheptanes are practically normal, it is noted that the expected exaltation of the molecular refraction normally caused by conjugated double bonds is not observed in the case of cyclopentadiene, cyclohexadiene, and cycloheptadiene. Still greater differences are observed between the cyclic and acyclic conjugated

[66] Wallach, *Goettingen Nachr.* October, 1910.
[67] Haworth, Prekin & Wallach, *J. Chem. Soc. 99,* 123 (1911).
[68] Perkin, 8th *Int. Cong. Appl. Chem.* VI, 244.
[69] Haworth & Fyfe, *J. Chem. Soc. 105,* 1662 (1914).
[70] *Ann. 415,* 98 (1918).

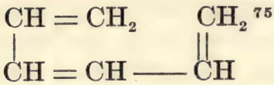
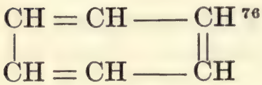
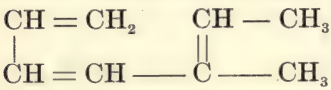
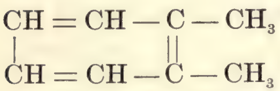
trienes, the exaltation being particularly great for the acyclic hydrocarbons but very slight in the case of the cyclic conjugated trienes. It was this fact which caused so much doubt and controversy over the constitution of $\Delta^{1,3}$-cyclohexadiene. The chemical evidence leaves no room for reasonable doubt regarding the constitution of this hydrocarbon and that it is by no means an exception will be seen from the following table, $E\ M_\alpha$ and $E\ M_D$ being the difference between the observed and calculated values for the α hydrogen and sodium D lines respectively.

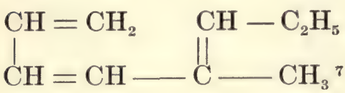
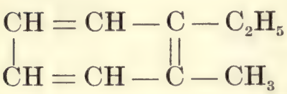
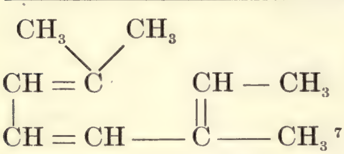
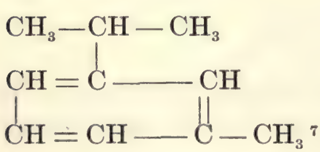
	$E\ M_\alpha$	$E\ M_D$
	+ 1.81	+ 2.10 [71]
	— 0.45	— 0.47 [72]
	+ 1.96	+ 2.03 [71]
	+ 0.02	+ 0.05 [73]
	.....	1.62 [74]
	+ 0.50	.....

The introduction of alkyl groups causes a definite exaltation of the molecular refraction as compared with the unsubstituted hydrocarbon.

The differences in the following series of trienes are particularly noteworthy, Auwers representing benzene as cyclohexatriene,

[71] *Ber.* *49*, 833 (1916).
[72] Auwers, *Ber.* *45*, 3077 (1912).
[73] Harries, *Ber.* *45*, 809 (1912) ; Willstätter & Hatt, *Ber.* *45*, 1647 (1912).
[74] *J. prakt. Chem.* (2) *82*, 74 (1910).

	$E\,M_\alpha$	$E\,M_D$
 [75]	+ 2.90	.....
 [76]	— 0.18	— 0.18
	+ 4.07	+ 4.34
 [76]	+ 0.20	+ 0.19

	$E\,M_\alpha$	$E\,M_D$
 [77]	+ 3.89°	+ 4.19
	+ 0.06	+ 0.05
 [77] (allo-ocimene)	+ 3.99	+ 4.29
 [78]	+ 0.30	+ 0.31

Just as a ketone or aldehyde group, in conjugated position with reference to a cyclopropane group, produces abnormally high refrac-

[75] Auwers & Eisenlohr, *J. prakt. Chem.* (20) *84*, 40 (1911).
[76] Landolt & Jahn, *Z. Physik. Chem.* *10*, 303 (1892).
[77] Enklaar, *Rec. trav. chim.* *36*, 215 (1917).
[78] Landolt & Jahn, *Z. physik. Chem.* *10*, 303 (1892).

tivity, a similar effect is produced by ketone and ethylene groups in conjugated positions, for example,

	M_α *Observed*	*E M* *Calc.*	ɒ
Crotonaldehyde, $CH_3CH=CH.C\begin{smallmatrix}\diagup H\\ \diagdown\!\!\diagdown O\end{smallmatrix}$	21.29	20.24	1.05
Mesityl oxide $(CH_3)_2C=CH.C\begin{smallmatrix}\diagup CH_3\\ \diagdown\!\!\diagdown O\end{smallmatrix}$	30.13	29.39	0.74
Carvenone,	46.52	45.82	0.70
Menthenone,	46.78	45.82	0.96

Aliphatic conjugated dienes *usually* show exaltation, as in 2.4-hexadiene E $M_\alpha = 0.98$ isoprene, E $M_D = 1.03$ [79] and hexatriene E $M_\alpha = 2.06$.

As noted above, unsaturated cyclic hydrocarbons containing two or more alkyl side chains and conjugated double bonds usually show exaltation, as in α-phellandrene and α-terpinene.[80]

$M\alpha$,
calc. = 44.97
obs. = 45.35

α-phellandrene

M_D
calc. = 45.24
obs. = 46.15

α-terpinene

Opinions differ as to whether a study of refractivity has really contributed much to the elucidation of the constitution of substances such as α-terpinene, and as to whether or not the evidence of such physical constants can be relied upon. Usually, as in the case of the terpinenes, our most trustworthy evidence has resulted from

[79] Calculated from recent data of Harries, *Ber.* 47, 1999 (1914), using $n^{16.5}_D$ 1.42617 and $d^{16.5°}_{4°}$ 0.6867 gives M_D 25.38; calculated 24.35.

[80] Auwers, *Ber.* 42, 2404, 2424 (1909).

chemical investigation.[81] In this connection it should be noted that certain substances in which considerable exaltation might be expected, show only the normal refractivity, as, for example, cyclooctatetrene discovered by Willstätter.[82]

$$\begin{array}{l} HC=CH.CH=CH \\ | \qquad\qquad\qquad\quad | \\ HC=CH.CH=CH \end{array} \qquad n_D^{20^\circ}\ 1.53460 \qquad \begin{array}{ll} \text{calc. } C_8H_8/\overline{=}4 & 35.07 \\ \text{obs.} & 35.20 \end{array}$$

This hydrocarbon has all the chemical properties which one would expect such a substance to have and yet benzene, having quite different chemical properties also shows only very slight exaltation, M_D observed 25.93, calculated for $C_6H_6/\overline{=}3$ 26.25. Wallach has urged caution in interpreting refractivity values and conclusions thus drawn are of doubtful value unless supported by other good evidence and assurance that the substance examined is of the highest purity. Thus, methyl heptenone on condensation yields a material which for a long time was considered, from its analysis and refractivity value, to be dihydroxylene. This has been shown, however, to be a *mixture* of xylene and tetrahydroxylene.[83] Early in the study of refractivity Brühl stated that the refractive index showed that the terpenes, $C_{10}H_{16}$, in orange peel oil, lemon oil and bergamot were identical and that the chemical evidence was merely confirmatory but not necessary to prove this fact. Wallach [84] pointed out that on such grounds Brühl should have claimed the identity of limonene and sylvestrene, since their physical constants are practically identical.

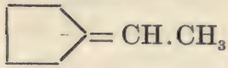
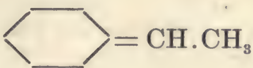
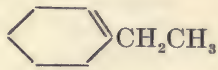
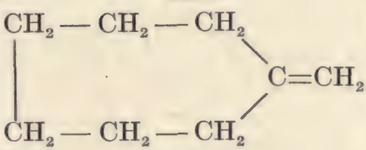
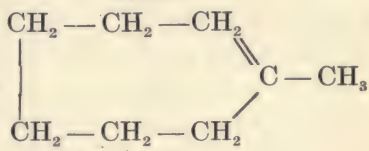
	Limonene, $C_{10}H_{16}$	*Sylvestrene, $C_{10}H_{16}$*
Boiling-point	175°–176°	174°–176°
d^{20°	0.845	0.847
n_D	1.4746	1.477
M_D	45.23	45.08

The close agreement of these constants is to be expected from the constitution of these hydrocarbons *q. v.*

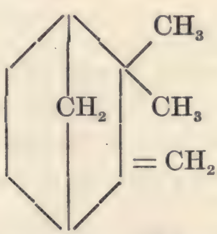
Wallach [85] has called attention to the fact that hydrocarbons having a semicyclic double bond show abnormally high refractivity.

[81] Wallach, *Ann.* *350*, 142 (1906); *374*, 224 (1910).
[82] *Ber.* *44*, 3423 (1911).
[83] Wallach, *Ann.* *395*, 76 (1913); *396*, 273 (1913).
[84] *Ann.* *245*, 191 (1888).
[85] *Ann.* *345*, 142 (1906); *360*, 34 (1908).

MOLECULAR REFRACTION

Calculated	Observed	Observed
		
31.83	32.12	31.89
		
31.83	32.26	31.8
		
36.43	36.82	36.52
		
41.03	41.56	41.02
		
36.43	36.64	36.43

Similarly the terpenes, terpinolene, sabinene, d.l.fenchene, β-terpinene and β-pinene have been shown by chemical investigation to have semicyclic double bonds, $>C=CH_2$, and the exaltations of their specific refractions due to this group vary from 0.3 to 0.5. Auwers [86] therefore argues that camphene must have the constitution proposed by Wagner since the exaltation of the molecular refraction (MD) of camphene is 0.51.



M_D 44.02 : calc. 43.51

camphene (Wagner)

[86] *Ann.* 387, 240 (1912).

Here also, however, the chemical evidence is much more convincing that camphene has the structure shown.[87]

The refractive index has been of very little value in the examination of commercial hydrocarbon oils. Rittman and Egloff,[88] give the results of the examination of corresponding fractions of seventeen different petroleums, five from California, four from Pennsylvania, five from Oklahoma, two from Russia and one from Mexico. As one would expect from what is known of the different types of hydrocarbons present in different petroleums, the refractive indices varied within wide limits.

Fraction	*Refractive Indices*
To 100°	1.375 to 1.423
100°–150°	1.407 to 1.434
150°–200°	1.425 to 1.448
200°–250°	1.437 to 1.465
250°–300°	1.449 to 1.493

The refractive indices were found to vary as the specific gravities.

The refractive index is usually determined in the examination of essential oils but the so-called "constants" obtained are of no value as evidence of adulteration unless supported by other good evidence.[89]

It is well known that the refractive index of a substance varies with the wave length of the light employed, light of short wave length giving the greater refraction. The *dispersion* or difference in the refraction of two different wave lengths, for example, the α and γ hydrogen lines, may be measured and the specific and *molecular dispersivities* calculated.[90] However such determinations can hardly be carried out except in a well equipped physical laboratory and the results show little more than the refractivity for a single wave length, for example, the sodium D lines, a strong, nearly monochromatic and satisfactory light available in any laboratory.

Magnetic Rotation.

When a beam of polarized light is passed through a transparent substance placed between the poles of an electro-magnet, so that the light travels in a direction parallel to the lines of the magnetic field,

[87] Cf. Haworth & King, *J. Chem. Soc.* *105*, 1342 (1914); Buchner, *Ber.* *46*, 759, 2108 (1913); Lipp, *Ber.* *47*, 871 (1919); Komppa, *Ber.* *47*, 934 (1914).

[88] *J. Ind. & Eng. Chem.* 7, 759 (1915).

[89] Cf. Gildemeister & Hoffmann, Die Aetherischen Oele, Ed. II, Vol. I, 580 (1910).

[90] Cf. Auwers & Eisenlohr, *J. prakt. Chem.* (2) *82*, 70 (1910); Darmois, *Compt. rend.* *171*, 952 (1920); Falk, *J. Am. Chem. Soc.* *31*, 86, 806 (1909) shows that dispersion, $M_\beta - M_\alpha$ or $M_\gamma - M_\alpha$ is not affected by temperature.

the plane of the polarized light is rotated. The original discovery was made by Faraday, but has been thoroughly investigated by W. H. Perkin, who has shown that the magnetic rotatory power of a substance depends partly upon its constitution. Perkin has applied the method to the study of the constitution of certain hydrocarbons, but it has never been widely employed, probably on account of the fact that the apparatus required is rather costly and involved; that, as Faraday showed, the amount of rotation is proportional to the strength of the magnetic field; that a "series constant" must be employed which is different for each slight difference in constitution, e. g., 0.508 for normal paraffines and 0.631 for iso paraffines and unknown for most of the other possible isomeric types; that the "constant" increment for the double bond varies from 0.578 to 1.112 in different types of substances; that the effect of substitution may vary with each successive substituent as when substituting halogens. In spite of the very admirable and painstaking work of Perkin, which is of the greatest interest from a physical standpoint, the method has not proved of great value in the investigation of hydrocarbons and the reader is therefore referred to Perkin's original papers,[91] or to other sources[92] for further information in regard to it.

Optical Activity.

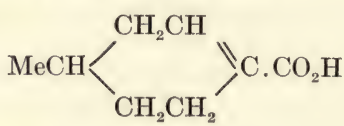
The majority of the terpenes occurring in nature are optically active. The degree of rotation of a particular terpene may vary practically from the one extreme value to the other, or from extreme lævo to dextro-rotatory power. Bacon[93] noticed that the rotatory power of specimens of phellandrene distilled from Manila elemi, collected from separate trees, varied from — 60.6 to + 126.0. Turpentine, chiefly α-pinene, varies in much the same way, though within smaller limits. The turpentine from American long leaf pine, *Pinus palustris*, is preponderatingly dextro rotatory, that from the Cuban pine, *Pinus heterophylla*, is usually lævo rotatory, and French turpentine, from *Pinus pinaster* is usually highly lævo-rotatory. In most cases, a particular species yields one or more terpenes whose optical activity is characterized by being strongly dextro or lævo-rotatory. Thus the Aleppo pine[94] of southern Europe yields a highly dextro α-pinene,

[91] *J. Chem. Soc. 69* (1896); *81*, 315 (1902); *89*, 849 (1906); *91*, 835, 851 (1907).
[92] Cohen, *Org. chem.* Vol. II, 44, Ed. II (1919). Smiles, *Relations between Chemical Constitution and Physical Properties*, 1910.
[93] *Philippine J. Sci. 4*, 96 (1909).
[94] Vezes, *Bull. Soc. chim.* (4) 5, 931 (1909).

$[\alpha]_D + 48.4°$, and α-pinene of extreme lævo rotation, $[\alpha]_D - 48.63°$, has been found in the essential oil of one of the species of eucalyptus.[95] Optically inactive pinene is much rarer but is found in American oil of peppermint, coriander and some lemon oils. In the case of limonene the dextro form is much the commoner variety and although the nature of racemic substances had long been understood, it was not until the discovery of l. limonene that Wallach was able to show that equal portions of d. and l. limonene yield the derivatives characteristic of "dipentene." Thus dipentene tetrabromide, melting-point 120°, is the racemic form of the d. and l.tetrabromides melting at 104°–105°.

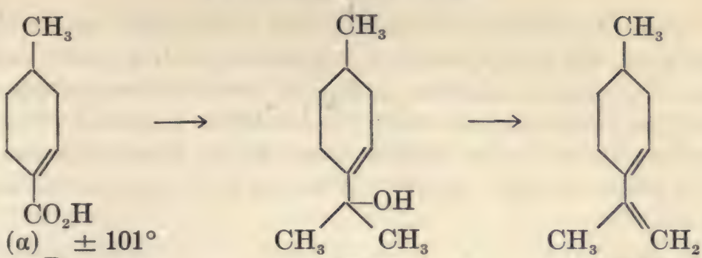
That heat tends to racemize optically active hydrocarbons is well known but in most cases distillation at atmospheric pressure, of the terpenes, does not appreciably affect the rotatory power. Bacon has noted that in the case of α-phellandrene exposure to direct sunlight causes comparatively rapid racemization.

When it is attempted to prepare optically active hydrocarbons by decomposing optically active alcohols, racemization occurs simultaneously and the resulting hydrocarbons are usually inactive. Perkin and K. Fisher decomposed terpineols by magnesium-methyl iodide in the *cold*, and also by heating with anhydrous oxalic acid but the resulting hydrocarbon was dipentene.[96] However, Perkin succeeded in preparing the isomeric hydrocarbon, $\Delta^{3.8(9)}$-p-menthadiene, in highly optically active form by resolving one of the intermediate products into its *d.* and *l.* forms. The acid

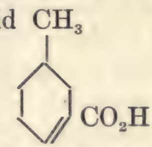


was resolved by means of brucine and strychnine to the *d.* acid $[\alpha]_D + 101.1°$ and *l.* acid $[\alpha]_D - 100.8°$. The ester of the lævo acid was then treated with magnesium-methyl iodide to form *l.*-Δ^3-p-menthenol(8) with the rotation $[\alpha]_D - 67.3°$. When the corresponding *d.* alcohol was treated in the cold with magnesium-methyl iodide the hydrocarbon was obtained and with the high rotation $+ 98.2°$.

[95] Smith, cf. Schimmel & Co. Bericht, 1899, I, 22.
[96] 8th *Int. Cong. Appl. Chem.* 6, 232 (1912).



$(\alpha)_D$ ± 101° ± 67.3° ± 98.2°

The isomeric m.menthadiene was also obtained in an optically active form by resolving the unsaturated acid  by means of *l*.menthylamine and subsequent reactions as in the case of the p.menthadiene.

The optical activity of petroleum, or more accurately, certain fractions of petroleum distillates, is one of the most significant facts bearing on the theory of the formation of petroleum from organic remains. According to Engler,[97] no oils which have been carefully examined are entirely without optical activity. Most petroleums are dextro-rotatory but a lævo oil has been reported from Borneo. Tschugaeff [98] called attention to the optical activity of a vaseline oil in 1904 and also stated the importance of this fact to the theory of organic origin. Rakusin [99] then reported dextro-rotatory fractions from American, Baku and Grossny oils. In 1835 Biot [100] had observed dextro-rotation in a "naphtha" of unknown origin but later observers all had regarded petroleum as optically inactive. Since 1904, however, many observers have confirmed the fact that certain fractions of petroleums are optically active. Crude petroleum cannot be measured for optical activity on account of the color and asphaltic matter which is frequently present.

Cholesterol yields oily decomposition products when subjected to destructive distillation [101] and wool grease yields optically active oils on decomposition, which led Marcusson [102] to attribute the optical activity of these oils and petroleum oils to decomposition products of

[97] *Ber.* *47*, 3358 (1914).
[98] *J. Russ. Phys.-Chem. Soc.* *36*, 453 (1904); *Chem. Ztg.* *1904*, 505.
[99] *J. Russ. Phys.-Chem. Soc.* *36*, 456 (1904); *Chem. Ztg.* *1904*, 505.
[100] *Mem. de l'acad. Sci.* *13*, 139 (1835).
[101] Windaus, *Ber.* *37*, 2027 (1904).
[102] *Chem. Ztg.* *1906*, 788.

cholesterol. Engler and his students have shown many points of similarity in the oils from cholesterol and optically active petroleum fractions. Thus when cholesterol is rapidly distilled the resulting oil is slightly lævo-rotatory and when this *l*.distillate is heated for several hours the rotatory power diminishes and finally becomes dextro rotatory; a closely parallel behavior is shown by the two lævo-rotatory Java oils.[103]

The chemical character of the optically active substance in petroleum has not been definitely shown. The naphthenic acids isolated from Baku oil are feebly active,[104] but oils which have been entirely freed from these acids show practically undiminished optical activity. Engler and his students have concentrated the optically active substance by repeated fractional distillation *in vacuo* until the most active fraction represented only 3 per cent of the original material but was unable to find indications of the presence of any substance other than hydrocarbons. Evidence that the optical activity of all petroleums is derived from a common original material, perhaps choleresterol, is afforded by the fact that the fractions of greatest degree of rotation, of the various petroleums examined, have approximately the same range of boiling-point, as is shown by the following table, which also shows the magnitude of rotation of these fractions after concentration by repeated distillation.

MAXIMUM OPTICAL ACTIVITY OF PETROLEUM FRACTIONS.[105]

Petroleum Source	*Fraction B.-P. °C*	*P mm.*	*Saccharimeter°*
Hanover	235–275	12	+ 10.4
Baku	230–278	12–13	+ 17.0
Galicia	260–285	12	+ 22.8
Roumania	250–270	12	+ 22.0
Pechelbronn	265–281	12.5	+ 7.6
Pennsylvania	255–297	14	+ 1.0
Java	268–281	15.5	+ 4.1

Optical activity has not been observed in petroleum fractions boiling below 200° at atmospheric pressure.

Specific Heat.

In 1831 Neumann discovered that in a series of compounds of analogous composition the specific heat varies inversely as the mo-

[103] See *cholesterylene*.
[104] Bushong & Humphrey, 8th *Int. Cong. Appl. Chem. 6,* 57 (1912).
[105] Engler, Das Erdöl, Vol. I, 202, 1913. For lævo-rotatory oil see Jones & Wootton, *J. Chem. Soc. 91,* 1146 (1907).

lecular weight. Mabery[106] determined the specific heats of a series of light fractions of Pennsylvania petroleum probably consisting of normal paraffine hydrocarbons. The uniform decrease in specific heat with increasing molecular weight suggests a constant relation analogous to the law of Neumann. In the following table the constant K is expressed in terms of the specific heat multiplied by the molecular weight and the product divided by the number of atoms in the molecule,

Hydrocarbon	*Molecular Weight*	*Specific Heat*	*No. of Atoms*	*K.*
C_6H_{14}	86	0.5272	20	2.26
C_7H_{16}	100	0.5074	23	2.21
C_8H_{18}	114	0.5052	26	2.21
C_9H_{20}	128	0.5034	29	2.22
$C_{10}H_{22}$	142	0.5021	32	2.23
$C_{11}H_{24}$	156	0.5013	35	2.23
$C_{12}H_{26}$	170	0.4997	38	2.23
$C_{13}H_{28}$	184	0.4986	41	2.24
$C_{14}H_{30}$	196	0.4973	44	2.23
$C_{15}H_{32}$	210	0.4966	47	2.24
$C_{16}H_{34}$	224	0.4957	50	2.23

Mabery also gives the latent heat of vaporization of the following hydrocarbons,

	Boiling-Point	*Heat of Vaporization in Calories*
Hexane	68°	79.4
Heptane	98°	74.0
Octane	125°	71.1
Cyclohexane	68°– 70°	87.3
Dimethylcyclopentane	90°– 92°	81.0
Methylcyclohexane	98°	75.7
Dimethylcyclohexane	118°–119°	71.7

From an industrial point of view data on the specific heats and heat of vaporization of various petroleum fractions are of value in order properly to design stills and condensers.[107] According to Troutons' rule the molecular heat of vaporization divided by the absolute boiling-point equals a constant, which is approximately 20. Graefe[108] points out that this relation can be employed to calculate the mean heat of vaporization of petroleum fractions (which distill at atmos-

[106] *Am. Chem. J. 28,* 66 (1902).

[107] In the early days of the American petroleum industry much of the apparatus employed was perfected and developed purely by the cut and try method. Karawajeff [*J. Soc. Chem. Ind. 32,* 128 (1910)] states that the average specific heat of heavy petroleum oils at 100°C is about 0.48, rising as a linear function of the temperature to about 0.60 at 400°C. For the specific heats at low temperatures see Bushong and Knight, *J. Ind. & Eng. Chem. 12,* 1197 (1920).

[108] *Petroleum 5,* 569 (1909) ; *Chem. Abs. 4,* 1362 (1910).

pheric pressure without decomposition). Graefe used a rather ingenious method for determining the mean molecular weight, i. e., lowering of the freezing-point of stearic acid. His results, calculated in this manner, are as follows:

Material	*Sp. Gr.*	*Average Mol. Wt.*	*Average B.-P.*	*Heat of Vaporize*	*Heat to Raise to B.-P.*	*Total Heat*
Light crude oil	0.883	113	216°	86.5	82	168.5
Gas oil	0.890	158	273°	69.2	107	176.2
Paraffine oil, light	0.920	190	328°	63.3	130	193.3
" " heavy ...	0.933	230	346°	53.8	138	191.8

Values, for petroleum distillates, determined calorimetrically usually fall within the range 130 to 190 calories.

Thermochemistry of the Non-benzenoid Hydrocarbons.

There is little question but that organic chemistry is too largely a compendium of methods of preparation, and, considering the meager equipment of many laboratories and the ease with which most organic reactions may be carried out, it was perhaps inevitable that this should be so. Also the difficulties in the way of understanding the theory or mechanism of organic reactions are manifold, and many factors other than thermochemical relations play very important rôles. Heat changes in organic reactions are often small and reactions frequently take place with the formation of substances which do not directly lead to increased entropy of the system; stereo chemical relations play an important part, many phases of which, for example the Walden inversion, we are far from understanding. The modification of the chemical properties of a given atom or element by neighboring substituents of pronounced chemical character is a factor which we know mostly in a qualitative way, in much the same way that a chef is familiar with the strength of his assortment of condiments. We know in a more or less quantitative way that a condition of stress in a molecule affects certain physical properties and endows the substance with unusual chemical activity, as for example cyclopropane. Thermochemical data have, as yet, been of very little assistance to organic chemists. Thus, according to Thomsen, ethylene oxide must have the structure $H_2C.O.CH_2$ "for the introduction of an atom of oxygen into the molecule of ethylene, in place of the double linkage, corresponds to a thermal effect of $93.98\text{-}73.47 = 20.51$ Calories, since the

taking up of an atom of oxygen by the ethane molecule in place of the single linkage produces a heat effect of 124.95–104.51 = 20.44 Calories. The relation is, therefore, exactly the same, and, if dimethyl ether has the composition $CH_3.O.CH_3$ *ethylene oxide must be dimethylene ether,* $CH_2.O.CH_2$. The view that ethylene oxide contained a single linkage between the carbon atoms $(CH_2—CH_2)$ would necessitate a heat

$$\begin{array}{c} (CH_2—CH_2) \\ \diagdown \quad \diagup \\ O \end{array}$$

of formation greater by 14.71 Calories, that is to say about 15 per cent higher than the experimental value."[109] No organic chemist would accept Thomsen's proposed structure of this substance in view of its many chemical reactions which point clearly to the ethylene oxide formula. Early in the use of the refractometer, Wallach cautioned Brühl that the refractive index should not be relied upon to decide questions of constitution unless well supported by chemical evidence and the history of such disputed cases has amply borne out Wallach's contention. Thus in the case of thermochemical evidence as to the constitution of benzene and other organic compounds, it should always be kept in mind that in the present state of our knowledge thermochemical data are evidence, not necessarily proof.

Also in many organic systems the mere number of reactions which are observed to take place precludes quantitative prediction, at least in the light of our present understanding. For example, in the pyrolysis of the simpler paraffine hydrocarbons we can calculate the thermal changes involved in a large number of reactions, some exothermic and others endothermic. One author has been criticised for employing the Nernst formula to calculate the reaction velocities of a large number of possible and impossible reactions of hydrocarbons at various temperatures, for example,

	K	K	K
	600°	750°	900°
$C + H_2 \longrightarrow CH_4$	0.077	0.012	0.003
$C_2H_6 \longrightarrow C_2H_4 + H_2$	0.0027	0.094	1.28

Experimentally it has been shown that ethylene is produced to a less and less extent as the temperature rises within this range, the percentage of ethylene after one minute being, at 675°, 24 per cent; at 810°, 11 per cent; at 1000°, 7 per cent.[110]

[109] Thomsen-Burke, Thermochemistry, *1908*, 453.
[110] Bone & Coward, *J. Chem. Soc. 93*, 1197 (1908).

As pointed out by Thomsen, the determination of the thermal effect which should result on formation of organic substances from their elements is particularly difficult, for only a few such substances can be so formed and these only under conditions which practically preclude such measurement. No satisfactory method is at present known for the measurement of these values, except determination of the heats of combustion. The heats of combustion of a number of hydrocarbons, as found by Thomsen, are given in the table below.

"The third column gives the heats of combustion, which in the case of non-gaseous bodies is given in the state of gas or vapor at 18°. In each case it is assumed that the products of combustion are cooled to 18°, and that consequently carbon dioxide and nitrogen appear as gases,—water, on the other hand, as a liquid."

"The fourth column gives the heats of formation of the products of the combustion; that is to say, the amount of heat which is evolved by the elements of the compound when they are burned in the free state, as, for instance, carbon to the dioxide, and hydrogen to water. *The heat of combustion of carbon is taken as 96,960 c. for each gram-atom of carbon, this being the heat of combustion of amorphous carbon. The heat of formation of water is 68,360 c. per gram-molecule.*"

"The *fifth* and *sixth* columns contain the heats of formation of the substances in the state of gas or vapor at 18°. This value is calculated from the heats of combustion according to the equation already given.

$$(C_a,\ H_{2b},\ O_c) \longrightarrow a(C,O_2) + b(H_2,O) - f(C_aH_{2b},O_c)$$

"The values calculated in this manner are the heats at formation at constant pressure. External conditions, however, exercise a certain influence on these values, since the products formed usually occupy a smaller volume than the sum of the volumes of the constituent elements. Thus 2 gram-molecules of hydrogen are required for the formation of 1 gram-molecule of CH_4; this corresponds, therefore, to a decrease in volume of 1 gram-molecule of hydrogen, or of 22,340 cubic centimeters, at 0° and 760 mm. pressure. Such a diminution of volume will result in the evolution of 543 c. at 0°, which corresponds to 580 c. at 18°. If now from the heat of formation of the compound we subtract 580 c. for each gram-molecular volume which has disappeared, we obtain the *heat of formation at constant volume.* It is this value, which is given in the sixth column of the following tables:

HYDROCARBONS.

Combustion: C_aH_{2b} $(2a + b)O\ aCO_2 + bH_2O$

Compound	Molecular Formula	Heat of Combustion of the gas at 18°	Heat of Formation of the products	Heat of Formation of the Compound at Constant pressure	Heat of Formation of the Compound at Constant volume
PARAFFINS.					
Methane	CH_4	211,930c.	233,680c.	21,750c.	21,170c.
Ethane	C_2H_6	370,440	399,000	28,560	27,400
Propane	C_3H_8	529,210	564,320	35,110	33,370
Trimethylmethane	$CH(CH_3)_3$	687,190	729,640	42,450	40,130
Tetramethylmethane	$C(CH_3)_4$	847,110	894,960	47,850	44,950
Diisopropyl	$(CH)_2.(CH_3)_4$	999,200	1,060,280	61,080	57,600
UNSATURATED HYDROCARBONS.					
Ethylene	C_2H_4	333,350	330,640	−2,710	−3,290
Propylene, normal	$CH_2{:}CH.CH_3$	492,740	495,960	+3,220	+2,060
Trimethylene	C_3H_6	499,430	495,960	−3,470	−4,630
Isobutylene	$CH_2{:}C{:}(CH_3)_2$	650,620	661,280	+10,660	+8,920
Isoamylene	$C_2H_4{:}C{:}(CH_3)_2$	807,630	826,600	+18,970	+16,650
Diallyl	$C_3H_5.C_3H_5$	932,820	923,560	−9,260	−11,580
Acetylene	$CH \vdots CH$	310,050	262,280	−47,770	−47,770
Allylene	$CH \vdots C.CH_3$	467,550	427,600	−39,950	−40,530
Dipropargyl	$C_3H_3.C_3H_3$	882,880	786,840	−96,040	−97,200

According to Thomsen isomeric organic substances may give identical heats of combustion, for example,

Allyl chloride, $CH_2 = CH.CH_2Cl$	454.68 Cal.
2-Chloropropylene $CH_2 = CHCl.CH_3$	453.37 Cal.

and the two isomeric dichloroethanes,

Ethylene chloride $CH_2Cl.CH_2Cl$	296.36 Cal.
Ethylidene chloride $CH_3CH.Cl_2$	296.41 Cal.

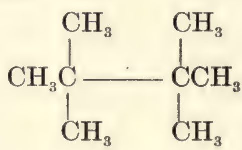
It should be pointed out that the chemical properties of these isomers differ widely, for example, the chlorine atom is much more stable or firmly bound in 2-chloropropylene than in allyl chloride, and ethylidene chloride is much more reactive to water and alkalies than ethylene chloride. However, T. W. Richards [111] has developed exceedingly accurate methods of calorimetry by which he has detected slight differences in the heats of combustion of five isomeric octanes, and it is, therefore, possible that Thomsen's conclusions regarding the identity of the heats of combustion of isomers such as the above may have to be modified. The differences in the heats of combustion for the octanes studied by Richards are considerably greater than the experimental error of his method of measurement. The values found by him are as follows,

[111] Richards & Jesse, *J. Am. Chem. Soc.* *32*, 268 (1910); *36*, 248 (1914).

Normal octane, liquid	5448	Kilojoules
2, 5 dimethylhexane	5442	"
2 methylheptane	5454	"
3.4 dimethylhexane	5444	"
3 ethylhexane	5439	"

Richards and Davis [112] find that the increase in the heat of combustion by substituting CH_3 for a hydrogen atom in a side chain is 648 ± 4 kilojoules, but when substituted for a hydrogen of the benzene nucleus the value is 638 kilojoules.

It is greatly to be regretted that so few thermal measurements of organic substances have been determined with the accuracy of Richards' measurements. It would be of interest to determine if the high degree of molecular symmetry of tetramethyl methane $C(CH_3)_4$ and 2,2,3,3,tetramethylbutane



which are characterized by abnormally high melting-points, show heats of combustion appreciably different from their normal isomers.

The effect of conjugation of double bonds upon the heat of combustion has been carefully investigated by Auwers, Roth and Eisenlohr.[113] A number of terpenes were used in the investigation and since empirical expressions for the determination of the "calculated values" of heats of combustion are not trustworthy, the average of the experimental values determined for limonene, *i*-limonene and sylvestrene, 1464 Calories was taken as a *normal* value for this terpene series. The values found for the molecular heats of combustion were as follows,

	Calories
d.-limonene [$\Delta^{1,8(9)}$-p-menthadiene]	1466
i-limonene	1462
sylvestrene [$\Delta^{1,8(9)}$-m-menthadiene]	1464
a-phellandrene	1434
a-terpinene	1428
d-*a*-pinene	1469
camphene (liquid)	1471
sabinene	1475

According to their results hydrocarbons having two conjugated double linkings have molecular heats of combustion about two per cent lower than the isomeric hydrocarbons containing two *non*-conjugated double

[112] *J. Am. Chem. Soc. 42,* 1599 (1920).
[113] *Ann. 373,* 267 (1910).

linkings. These "thermal depressions" are about of the same order of magnitude as the exaltations of molecular refractivity of such hydrocarbons. On account of the refined experimental technique required to make such thermal measurements with great accuracy, the thermal method will never displace the optical methods but may be helpful as an auxiliary in certain cases. Thermal measurements made in the course of this work support the contention that Semmler's carvenene is identical with α-terpinene. The parallelism between the thermal and optical data disappears in the case of the bicyclic terpenes. The heats of combustion of a number of cyclic hydrocarbons have been reported by Zuboff,[114] as follows, expressed as Calories per gram molecule, based on Regnault's determination of the specific heat of water,

Hydrocarbon		*Heat of Combustion*	
Formula	*Name*	*At Const. Vol.*	*At Const. Pres.*
C_6H_{14}	Normal Hexane	997.8	999.8
C_6H_{12}	Methylcyclopentane	945.7	947.4
"	Cyclohexane	943.4	945.1
C_7H_{14}	1.3 Dimethylcyclopentane	1099.5	1101.5
"	Methylcyclohexane	1100.8	1102.8
"	Cycloheptane	1096.3	1098.3
C_8H_{16}	1.1 Dimethylcyclohexane	1252.8	1255.1
"	1.3 " "	1248.1	1250.4
"	1.4 " "	1238.9	1241.2
C_9H_{18}	1.3.3 Trimethylcyclohexane	1406.0	1408.6
C_7H_{12}	Methylcyclohexene, α	1047.6	1049.3
"	" β	1053.2	1054.9
"	Cycloheptane	1058.7	1060.5

Roth and Auwers[115] have criticised the technique of Stohmann's earlier work and point out that many of the hydrocarbons investigated by Stohmann very probably were impure. They have redetermined the heats of combustion of a series of benzene and cyclohexane derivatives which were most carefully purified. Their results differ somewhat from Stohmann's and their results show that the increase in the heat of combustion produced by the addition of two hydrogen atoms to the aromatic hydrocarbon is much greater than that due to the addition of hydrogen to the dihydro and tetrahydro compounds; the latter two increases also are not the same. The difference between the heats of combustion of a conjugated cyclohexadiene and the corresponding aromatic hydrocarbon is about 64 Calories. The difference between that of a conjugated cyclohexadiene and the cyclohexene is about 50 Calories, and the difference between the cyclohexene and the

[114] *J. Russ. Phys.-Chem. Soc. 33,* 708 (1901).
[115] *Ann. 407,* 145 (1915).

cyclohexane is about 45 Calories. In the case of simple acyclic olefines the difference between the saturated and unsaturated substance is about 37 Calories and Roth and Auwers state that hydrogenation appears always to be an exothermic reaction. The following values (Calories) are the molecular heats of combustion at constant pressure and at the specified initial temperature.

Substance	*Calories*	*Temp.*
benzene	782.3	20.4°
cyclohexene	893.7	21.0°
cyclohexane	938.5	17.4°
toluene	935.2	19.0°
1-methylcyclohexene	1049.6	15.7°
m-xylene	1089.5	20.6°
1.4-dimethyl-$\Delta^{1\cdot 3}$-cyclohexadiene	1153.7	19.5°
1-ethylcyclohexene	1205.4	14.9°
1-methyl-4-ethyl-$\Delta^{1\cdot 3}$-cyclohexadiene	1312.5	20.0°
1-methyl-4-isopropyl-$\Delta^{1\cdot 3}$-cyclohexadiene	1472.2	20.5°
naphthalene (solid)	1235.2	....
" (liquid)	1239.7	....
Δ^{1}-dihydronaphthalene	1297.8	20.5°
Δ^{2}- " (solid)	1299.8	20.7°
" " (liquid)	1302.7	....
1.2.3.4.tetrahydronaphthalene	1341.2	20.0°
decahydronaphthalene	1503.9	19.2°

The heat energy represented by the single bond carbon to carbon $>\!C - C\!<$ may be ascertained by reference to the heats of combustion of the paraffine series and the intramolecular energy of H_2, the hydrogen molecule. Richards and Jesse[116] showed, in a series of unusually accurate determinations on very carefully purified octanes, that the mean value for the octanes, C_8H_{18} is 1299.9 Calories.

The average value for CH_2 is 156 Calories. The heat of combustion of carbon and of hydrogen in hydrocarbons of the paraffine series may be determined by the simultaneous equations shown below, using the heats of combustion of ethane and propane found by Berthelot and Matignon,[117] X being the heat of combustion of a carbon atom and Y the heat of combustion of a hydrogen atom,

$$C_2H_6, \quad 2X + 6Y = 370.9 \text{ Calories}$$
$$C_3H_8 \quad 3X + 8Y = 526.7 \quad \text{"}$$

From these equations $X = 96.5$ Calories and $Y = 29.65$ Calories: also if we take $X + 2Y = 156$ together with the mean octane value 1299.9 Calories, then, in round figures, $X = 96$ and $Y = 30$ Calories.

[116] *J. Am. Chem. Soc.* *1910*, 292.
[117] *Ann. chim. phys.* (6) *30*, 547 (1893).

Since this value is an additive one, it follows that the energy of dissociation of C-H and C-C bonds are practically equal, or within the limits of experimental error; for example, if there were a noticeable difference between the heat of dissociation, or rupture, of C-H and C-C, then the factor would be very different for C_2H_6, having 6 C-H bonds and *one* C-C bond, than with C_8H_{18}, having 18 C-H bonds and seven C-C bonds.

As noted above hydrogen in the paraffine hydrocarbons has a heat of combustion of 30 Calories; by burning hydrogen gas, however, the molecular heat of combustion is not 2 x 30 or 60 Calories but 67.5 Calories. This difference, 7.5 Calories, can be due only to the greater intramolecular energy of the hydrogen molecule. Langmuir [118] and Isnardi [119] have calculated the heat of dissociation of hydrogen from other observations and both agree on the value 90 Calories for higher temperatures and Nernst [120] has calculated that at absolute zero the value would be about 100 Calories. Using Nernst's value the heat of dissociation of the carbon-hydrogen bond, and also the carbon-carbon single bond, is

$$100 - 7.5 = 92.5 \text{ Calories.}^{121}$$

A second carbon-to-carbon bond as in ethylene, $H_2C = CH_2$. has a much smaller heat of dissociation. Thus for ethylene:

Calculated, C_2H_6, $2 \times 96 + 4 \times 30 =$	312	Calories
Found by Berthelot [122]	340	"
Found by Mixter [123]	344.6	"

The increase for the double bond is, according to these observations, 28 to 32.6 Calories, and the differences between the observed values and those calculated in the same manner in the case of other olefines, agree very well with the above values, for example,

Propylene, calculated	468.0 Cal.
Propylene, found (Berthelot)	497.9 Cal.
Difference	29.9 Cal.
Hexylene, calculated	936.0 Cal.
Hexylene,[124] liquid, 959.9 Cal., and adding 7.8 Cal. for heat of vaporization........	967.7 Cal.
Difference	31.7 Cal.

[118] *Z. Elektrochem.* **23**, 242 (1917).
[119] *Z. Elektrochem.* **21**, 416 (1915).
[120] Die Grundlagen des neuen Wärmesatzes, *1918*, 153.
[121] Weinberg, *Ber.* **52**, 1501 (1919).
[122] *Ann. chim. phys.* (6) **30**, 557 (1893).
[123] *Chem. Zentr.* *1901* (2), 1250.
[124] Zübow, cf. Landolt & Börnstein, Physikalische Tabellen, Ed. *1912*, 909.

The mean value for the increase in the molecular heat of combustion of simple olefines is therefore about 30 Calories greater than the value calculated from the number of carbon and hydrogen atoms contained in the hydrocarbon. In the case of conjugated diolefines, however, the difference between the observed and calculated values is not $2 \times 30 =$ Calories, *but a very much smaller value,* for example,

$\Delta^{2\text{-}4}$-Hexadiene	
Calculated $(6 \times 96 + 10 \times 30)$	876.0 Cal.
Observed[125] $884.7 + 7.6$	892.3 Cal.
Difference	16.3 Cal.

Other differences of the same order, between the observed and calculated values for the dienes, have been observed.[126]

Dielectric Constants: The electrical insulating value of the paraffines, and refined mineral oils generally, is taken advantage of in the utilization of oils for transformers, and the use of paraffine in impregnating the cotton insulation of wires carrying low voltage currents. The dielectric constant of paraffine wax has been referred to under this head. This very property which makes these hydrocarbon oils valuable as insulating material is a source of considerable danger in the case of the more volatile mineral oils of low flash point since they easily become electrostatically charged by friction, as by being pumped through a pipe, or agitating woolen goods in a gasoline cleaning mixture. Electrical spark discharges caused in this way have resulted in many disastrous explosions and fires. Holde[127] states that light petroleum oils can easily acquire a charge amounting to several thousand volts by being pumped through a metal pipe. Even when the pipes and containers are grounded it is possible that, in the case of such good insulators, the electrical charge cannot be sufficiently rapidly dissipated. Holde gives the specific conductivity of "light petroleum" as 10^{-14} to 10^{-15}. Decrease of the dielectric constant with rise in temperature is very small, the temperature coefficient for cyclohexane being 0.00078.

Viscosity.

Measurements of viscosity have been of value as evidence of molecular association, the formation of hydrates in aqueous solution, the existence of racemic liquid substances and Dunstan and

[125] Roth & Moosbrugger, *Ann.* *407*, 153 (1915).

[126] The effect of conjugation of double bonds on the heat of combination is of particular interest in connection with the constitution of benzene. Cf. Weinberg, *Ber.* *52*, 1501 (1919).

[127] *Ber.* *47*, 3239 (1914).

Thole [128] have noted certain facts which indicate that this property is to a certain extent influenced by the constitution, of organic substances. From the few facts which are known, it appears that the normal paraffines pentane, hexane, heptane and octane, have slightly greater viscosities than their branched chain isomers.[129] Ortho-xylene has a greater viscosity than *meta* or *para*-xylene, but the viscosities of a number of isomeric non-benzenoid hydrocarbons have never been compared. Alicyclic hydrocarbons have greater viscosities than paraffines of the same boiling-point but as to the constitution of mineral lubricating oils practically nothing is known.

Viscosity decreases rapidly with rise in temperature and the curves are apparently hyperbolic.[130]

The relation between viscosity and lubrication has been reviewed by Mabery and Mathews,[131] who point out that while viscosity is generally accepted as a standard of value in classifying lubricating oils, it is not certain that it is reliable as indicating the durability and wearing qualities of oils differing widely in composition. The viscosity of lubricating oils has received considerable attention from engineers and analysts and many forms of apparatus have been proposed for its determination, but these instruments all give arbitrary values, which are the resultants of several factors, of which viscosity is one. Most of these instruments measure the rate of flow of the oil through an orifice and the interpretation of the results is based upon the assumption that the flow of oil through an orifice is a correct measure of surface viscosity between bearing surfaces. Mabery and Mathews obtained a set of relative values for the specific viscosity of hydrocarbons obtained by fractional distillation of petroleum. They employed Ostwald's method in which the oil is made to flow through a capillary tube under a definite pressure. The various fractions had approximately the composition indicated by the formulæ.

Hydrocarbon	*Boiling-Point*	*Sp. Gr.*	*Spec. Viscosity at 20°*
C_7H_{16}	98°–100°	0.724	0.51
C_8H_{18}	125°	0.735	0.60
$C_{10}H_{22}$	172°–173°	0.747	0.96
$C_{12}H_{26}$	212°–214°	0.769	1.49
$C_{15}H_{32}$	158°–159° (50mm.)	0.793	2.79
$C_{16}H_{34}$	174°–175° "	0.799	3.35
$C_{18}H_{38}$	199°–200° "	0.813	5.97

[128] Cauwood & Turner, *J. Chem. Soc. 107*, 276 (1915).
[129] Thorpe & Roger, *Phil. Trans. 185A*, 397 (1894); *189A*, 71 (1897).
[130] Bingham & Harrison, *Z. physik. Chem. 66*, 1 (1909). Dunstan and Stevens have determined the viscosities of a number of typical lubricating oils at temperatures within the range 70°-200°C and plotted the results in curves. *J. Soc. Chem. Ind. 30*, 1063 (1921).
[131] *J. Am. Chem. Soc. 30*, 992 (1908).

That the paraffines have markedly lower viscosities than the cyclic hydrocarbons of the same boiling-point is shown by the following, determined at 60°.

Series	*Boiling-Point*	*Sp. Gr.*	*Spec. Viscosity*
C_nH_{2n+2}	274°–276° (50mm.)	0.775	8.51
C_nH_{2n-2}	274°–276° "	0.835	15.63
C_nH_{2n+2}	294°–296° "	0.781	10.88
C_nH_{2n-2}	294°–296° "	0.841	21.23

The marked effect of ring closing and the very slight effect of unsaturation is also shown by the following comparative values found by Thole.[132]

Substance		$\eta 25°$	$\frac{\eta}{M^2} \times 10^7$
Hexane	$CH_2-CH_2-CH_3$	0.00311	4.2
Cyclohexane	$CH_2-CH_2-CH_2$ $\vert \qquad\qquad \vdots$ $CH_2-CH_2-CH_2$	0.00894	12.6
Methylbutyl ketone	CH_2-CH_2-CO	0.00584	5.8
Cyclohexanone	CH_2-CH_2-CO $\vert \qquad\qquad \vert$ $CH_2-CH_2 \,..\, CH_2$	0.0280	29.1
Methylamyl ketone	$CH_2-CH_2-CH_2-CO$	0.00766	5.9
Cycloheptanone	$CH_2-CH_2-CH_2-CO$ $\vert \qquad\qquad\qquad \vert$ $CH_2-CH_2 \,.........\, CH_2$	0.0259	20.6
Hexane		0.00311	4.2
Diallyl	$CH_2=CH.CH_2\ CH_2CH=CH_2$	0.00269	4.0
Isopentane[133]	$(CH_3)_2CH.CH_2CH_3$	0.00223	4.3
Trimethylethylene	$(CH_3)_2C=CH.CH_3$	0.00212	4.3
Isoprene	$CH_2=C(CH_3).CH=CH_2$	0.00214	4.6

Removal of paraffine wax improves the viscosity of lubricating oils, as is shown by the following data of Mabery and Mathews.

INFLUENCE OF SOLID PARAFFINE ON VISCOSITY AT 20°.

Hydrocarbon	*Boiling-Point (50mm.)*	*Sp. Gr.*	*Specific Viscosity*
(a) Penn. distillate C_nH_{2n-2} cooled to —10° and filtered	312°–314°	0.868	88.16
(a) + 2.5% solid paraffine of same boiling-point	312°–314°	0.868	82.30
(b) Penn. distillate C_nH_{2n-2} cooled to —10° and filtered	276°–278°	0.861	37.57
(b) + 2.5% solid paraffine of same boiling-point	276°–278°	0.860	36.39

It is generally recognized that the real function of oil in lubrication is to maintain a liquid film between the moving metal surfaces.[134] Under pressure the tendency is for the oil to be squeezed out and the

[132] *J. Chem. Soc.* *105*, 2004 (1914).
[133] Thorpe & Rodger, *Phil. Trans.* *185A*, 570 (1894).
[134] f. Ubbelohde, *Petr. Rev.* *27*, 293, 325 (1912).

oil film broken; the cohesion of the oil film itself and its tendency to wet or adhere to the metal surface and its ability to penetrate interstices by capillarity are factors of prime importance. While these factors may not be generally recognized, viscosity has come to be considered in a general way as a measure of the resistance to the breaking down of the oil film. Jerome Alexander[135] uses the expression "film" to denote a layer of fluid on the solid surface of the order of 10^{-7} centimeters in thickness and states that with a true lubricant the facility of slipping is maximal when a layer of such excessive tenuity separates the solid faces and nothing is gained by increasing the thickness of the layer, a fact experimentally demonstrated with castor oil. According to Alexander, lubrication depends wholly upon the chemical constitution of a fluid, and the fact that the true lubricant is able to render slipping easy when a film of only about one molecule deep is present on the solid faces, suggests that the true lubricant is always a fluid which is adsorbed by the solid face. Alexander explains the superior lubricating power of graphite in oil by the formation of a graphite surface on the metal to which the oil adheres more strongly and greater pressure is therefore required to break down this oil film. Similar views, supported by experimental evidence, have been expressed by Stanton, Archbutt and Southcombe[136] and by D. R. Mountford.[137] The latter believes that the molecules of the liquid enter into a firm "physico-chemical" union with the metallic surfaces (or "adsorption" according to Alexander). Using a friction testing machine of the Thurston type the friction coefficient of a certain mineral oil was reduced from 0.0065 to 0.0042 by the addition of 2 per cent of fatty acids. The experiments of the former authors were carried out at the National Physical Laboratory and they conclude that viscosity is not the only or the most important factor in cases of difficult lubrication. They also attribute "oilness" to adhesion or chemical (?) affinity between the metal and the lubricant. In their experiments one per cent of the fatty acids of rape oil added to a mineral oil lowered the friction coefficient from 0.0047 to 0.0033 and 60 per cent of neutral rape oil was necessary to produce the same effect.

Widespread dissatisfaction exists with the present methods of testing employed to determine the lubricating value of oils and Dunstan

[135] *J. Ind. & Eng. Chem. 12,* 436 (1920).
[136] *Engineering, 108,* 758 (1919); *Chem. Abs. 14,* 491 (1920).
[137] *Proc. Phys. Soc. London 32,* II, 1 (1920); *Chem. Abs. 14,* 1475 (1920); Wells & Southcombe, *J. Inst. Petr. Techn. 4,* 219 (1918).

and Thole [138] have recently expressed the opinion (shared by the present writer), that no method has yet been developed which gives values which express rationally or accurately the lubricating value of an oil. The friction testing machine of Thurston is designed to duplicate closely conditions actually obtaining in practice, but the friction coefficients so obtained are strictly a function of the viscosity and, as pointed out by Ubbelohde, are superfluous if the viscosity is determined. A device for testing *film stability* under variable pressure and movement of surfaces would appear to be rational and might do much to clarify understanding of this subject.

It is commonly stated that pressure has no effect upon viscosity but under very great pressures the viscosity of mineral oils is greatly altered. Under a pressure of 5 tons per square inch the viscosity of mineral oils increases 16-fold, and Bridgeman [139] noted that ordinary lubricating oils become very viscous at pressures of a few thousand atmospheres, and kerosene at 10° and 8,000 atmospheres changes to about the consistency of vaseline. The viscosity of mineral and fatty oils increases with pressure and at pressures greater than 800 kilograms per square centimeter the rate of change is very great. At 1,000 kg. per sq. cm. mineral oils have viscosities ten to twenty-five times the viscosities at ordinary atmospheric pressure.[140]

Solubility: Most petroleums and their distillates are completely miscible in benzene, carbon bisulfide, ether and chloroform. Absolute alcohol does not dissolve crude petroleums completely but amyl alcohol dissolves the hydrocarbons, leaving asphaltic matter undissolved. Petroleums containing relatively large proportions of aromatic hydrocarbons are dissolved by solvents such as alcohol to a larger extent than other petroleums. Oils containing a maximum proportion of paraffine hydrocarbons, such as light Pennsylvania oil, are generally least soluble. The lighter fractions are more soluble than the higher boiling fractions. In the following table the "critical solution temperature" was determined by heating the distillate with an equal volume of the solvent, then cooling slowly and noting the temperature at which turbidity appeared.[141]

[138] *J. Inst. Petr. Techn. 4*, 191 (1918).
[139] *Proc. Am. Acad. 47*, 345 (1911).
[140] Hyde, *Proc. Roy. Soc. 97A*, 240 (1920).
[141] Chercheffsky, *J. Petr. 1910*, 210.

Petroleum	Sp. Gr. of Fraction	Crit. Sol. Temperature °C ethyl alc. 96.5%	Crit. Sol. Temperature °C acetic anhydride
American	0.780	50.°	78.5
(Pennsylvania)	0.800	68.5°	91.
	0.820	87.°	104.5
Russian	0.780	36.°	66.
	0.800	47.5°	72.
	0.820	60.°	79.5
Galician	0.780	31.°	60.
	0.800	53.°	75.5
	0.820	72.5°	89.5
Roumanian	0.780	miscible at 20°	53.
	0.800	30.°	57.
	0.820	42.°	63.5

Although paraffine wax has been a common commercial product for a great many years and finds most varied application both in the industries and in scientific work, very little information has been published regarding its solubility in various solvents or its solvent power for other substances. The following table gives the solubility of a hard paraffine, melting-point 64°–65° (about 10° higher melting-point than that of the average commercial paraffine) which had been prepared from ozokerite. The softer waxes are probably more soluble than the sample here described.[142]

Solvent	g Paraffine Dissolved by 100 g.	100 cc.	Wt. of Solvent to Dissolve 1 Part Paraffine
CS_2	12.99	....	7.6
Light petr.— to 75 °C — Sp. Gr. 0.7233	11.73	8.48	8.5
Turpentine, 158°–160°	6.06	5.21	16.1
Xylene, commercial 135°–143°	3.95	3.43	25.1
Toluene, 108.5°–109.5°	3.92	3.41	25.5
Chloroform	2.42	3.61	41.3
Benzene	1.99	1.75	50.3
Ethyl ether	1.95	....	50.8
Acetone	0.262	0.209	378.7
Ethyl acetate	0.238	....	419.
Ethyl alcohol, 99.5%	0.219	....	453.
Amyl alcohol, 127°–129°	0.202	0.164	495.
Methyl alcohol	0.071	0.056	1447.
Methyl formate	0.060	....	1648.
Glacial acetic acid	0.060	0.063	1668.
Acetic anhydride	0.025	....	3956.
Formic Acid (cryst.)	0.013	0.015	7689.

A comprehensive discussion of the problem of separating paraffine wax from viscous oils by the use of solvents has recently appeared, the raw material investigated being the oily distillates obtained by the distillation of shales and lignites at low temperatures. In connec-

[142] Pawlewski and Filemonowicz, *Ber. 21*, 2973 (1888).

tion with this work the solubility of paraffine wax, melting-point 56°, was determined in mixtures of benzene and alcohol at ordinary temperatures and in the cold.[143]

Solubility of Paraffine: Grams in 100cc. Solvent.

Solvent	*23°C*	*0°*	*—20°*
Acetone	0.27	0.06	0.02
Benzene-alcohol, 2:8	0.48	0.10	0.01
" " 3:7	0.77	0.18	0.04
" " 4:6	1.14	0.23	0.05
Alcohol, 94.5%	0.16	0.01	0.006

Unsaturated hydrocarbons are generally more soluble than saturated hydrocarbons which fact is utilized in their separation by liquid sulfur dioxide. The hydrocarbons, including unsaturated hydrocarbons are very much less soluble in ethyl alcohol than alcohols, aldehydes, ketones and esters, which fact is made use of in the manufacture of terpene and sesquiterpene-free essential oils. Very few data bearing on this have been published but the solubility of turpentine and 95 per cent alcohol may be taken as a typical example of the solubility of this type of hydrocarbon.[144]

Temperature of Separation °C	*Grams of 95% Alcohol in 100 g. Mixture*	
20.7	2.4	oil rich phase
42.2	3.4	
53.0	7.2	
53.1	10.2	alcohol rich phase
44.0	20.3	
37.2	30.6	
29.6	48.3	
23.9	52.8	
16.3	61.4	
—15.5	76.6	
—24.	81.1	
—63.	87.1	

Hexane is miscible with methyl alcohol at 42.8°.[145] The effect of the hydroxyl group in diminishing the solubility of a substance in hydrocarbons explains the slight solubility of castor oil in lubricating oils. The solubility of castor oil in gasolene, which is of some technical importance, is very much like the behavior of aniline and the simpler paraffines. Castor oil is usually stated to be insoluble in gasolene but Atkins finds that it is miscible with isohexane at 40.8°, with octane at 47.8° and that it is miscible at ordinary tempertaures in certain gaso-

[143] Seidenschnur, *Brennstoffchem.* 2, 49, 73, 81 (1920).
[144] Vezes & Mouline, *Bull. soc. chim.* (3) *31*, 1043 (1904).
[145] Rothmund, *Z. physik. Chem.* *26*, 433 (1898).

lenes rich in naphthenes such as that from Roumanian and Galician petroleum.[146] Aniline and aliphatic hydrocarbons are miscible when warmed but separate into two phases when chilled. Thus amylene and aniline[147] are miscible at temperatures above 14.5°.

	Grams Aniline in 100 g.	
Tempo. °C	*Amylene Layer*	*Aniline Layer*
0.	19.5	81.5
4.	20.5	79.5
8.	24.2	75.8
10.	28.	73.
12.	34.	68.
14.	45.	59.
14.5	miscible	

The normal hydrocarbons, pentane, hexane, heptane and octane, are miscible with aniline[148] at 72°, 69°, 70° and 72° respectively, cyclopentane at 18° and cyclohexane at 31°.

Crude petroleum oils contain considerable dissolved methane, ethane and propane and on heating or distilling the oil these dissolved gases are not immediately expelled. Markownikow showed that kerosene and a sample of machine oil (Sp. Gr. 0.906) dissolved about 220 volumes of isobutylene at ordinary temperatures and that the gas was completely expelled only after heating to about 260°. Unsaturated gaseous hydrocarbons, ethylene and propylene are dissolved from oil gas by compressing with heavy oil to a greater extent than the saturated hydrocarbons which accompany these olefines in oil gas, and on heating or applying diminished pressure to the heavy oil solution the evolved gas is accordingly richer in olefines. Russian kerosene dissolves 0.144 volume of methane and 0.164 volume of ethylene at 10° and atmospheric pressure. McDaniel[149] has determined the solubilities of methane, ethane, and ethylene in ten organic solvents at temperatures from 20° to 60°. The solvents in the order of increasing solvent power for methane at 25° are methyl, amyl, ethyl, isopropyl alcohols, benzene, toluene, m-xylene, hexane and heptane. With ethane and ethylene the same solvents fall into a similar series in the same order. Contrary to Just[150] McDaniels finds that the solubilities of these solvents for nitrogen, oxygen and carbon dioxide do not follow in the same order as in the case of the hydrocarbons. Ethylene is more soluble in water than in kerosene[151] (water dissolves 0.149

[146] *J. Inst. Petr. Technologists, 6,* 223 (1920).
[147] Konowalow, *Ann. physik.* (4) *10,* 375 (1903).
[148] Chavanne & Simon, *Compt. rend. 168,* 1111 (1919).
[149] *J. Phys. Chem 15,* 587 (1911).
[150] *Z. physik. Chem. 37,* 342 (1901).
[151] Gniewosz & Walfisz, *Z. physik. Chem. 1889,* 70.

volumes of ethylene at 20°). According to Charitschkow,[152] carefully refined kerosene dissolves more ammonia at 22°, 0.4982 volumes, than at 0°.

The *solvent* power of compressed gases for certain solids and liquids having very low vapor pressures is a fact frequently overlooked. A compressed gas has noticeable solvent power for such a solid or liquid only when the gas compressed to the liquid state is of such a character as to dissolve the solid or liquid to a marked degree, and when one recalls that the physical properties of gas and liquid become identical at the critical point it becomes evident that the solubility curves of gas and liquid must merge smoothly into each other at the critical point. Ethyl chloride dissolves in 5 to 6 volumes of methane under 180 atmospheres pressure, at 17°, and at 200 atmospheres the two become miscible and the surface separating gas and liquid phases disappears. Iodine, camphor and *paraffine wax* dissolve in compressed methane to a marked extent and on releasing the pressure the paraffine wax is deposited again. Compressed ethylene also has a very marked solvent power for paraffine wax and stearic acid.[153]

Cyclohexane has been proposed as a cryoscopic solvent but is unreliable for this purpose on account of the tendency of substances containing hydroxyl, carboxyl, carbonyl or nitro groups to associate in this solvent.[154] Iodine is less soluble in cyclohexane than in benzene.[155]

Hexane generally has less solvent power than benzene. One hundred grams of the former dissolves 0.37 grams of anthracene at 25°, as compared with 1.86 grams in benzene. Ligroin, 100 g., dissolves 0.72 g. benzoic acid at 16° and turpentine dissolves 5.09 grams (at 25°). Sulfur is markedly soluble in hexane, as indicated in the following table,

SOLUBILITY OF SULFUR IN HEXANE.[156]

Temp. °C	*g.S. in 100 g. Solution*
—20	0.07
0	0.16
20	0.25
40	0.55
60	1.0
80	1.7
100	2.8
120	4.4
130	5.2
140	6.0

[152] *Trudi Bakuer Techn. Ges. 1893*, 5; Gurwitsch (Wiss. Grundl, d. Erdölbearb, *1913*, 100.
[153] Villard, *Chem. News*, *78*, 297, 309 (1898).
[154] Mascarelli, *Atti accad. Lincei* (5) *17*, 494.
[155] Bruni, *Gazz. chim. Ital. 42*, 12.
[156] Etard, *Ann. chim. phys.* (7) *2*, 526; *3*, 275 (1894).

The true solubility of sulfur in organic solvents is frequently difficult to determine on account of the fact that sulfur frequently forms colloidal solutions, as in the now well-known example of colloidal sulfur in β.β-dichloroethyl sulfide.[157] The solubility of sulfur in the hydrocarbon caoutchouc has been such a case, further complicated by the fact that, on warming, the sulfur is able to combine chemically with the double bonds of the hydrocarbon. Also, sulfur appears to be more soluble in organic substances containing one or more chemically bound sulfur atoms and Skellon[158] finds that as the per cent of chemically bound sulfur in vulcanized rubber increases, the solubility for sulfur as free sulfur increases. Thus ebonite may contain a greater proportion of free sulfur than soft cured rubber and still not bloom. Loewen[159] observed the solution of sulfur in rubber under a microscope and noted that when the time of "vulcanization" is short, droplets of melted sulfur are visible; on continued heating the mixture clears up and the droplets disappear but on cooling sulfur globules may reappear. If the time of heating be a little longer than in the last case, there is not sufficient free sulfur in solution to form droplets on cooling but crystalline sulfur may slowly separate on standing. If the time of vulcanization is still further prolonged, no free sulfur will separate after cooling.

The viscosities of rubber solutions in chlorinated solvents are approximately double the viscosities of solutions, of the same concentration, in gasolene or benzene, but, after heating, all kinds of rubber solutions have about the same viscosity.[160] Gaunt finds that the viscosities of fine hard Para rubber in various solvents, in order of decreasing viscosity, are as follows, benzene, $CHCl_3$, gasolene, ethyl ether.[161] Gaunt assumes that such rubber solutions contain aggregates of rubber micelles and that heating, mechanical working of the rubber or other processes which break up these aggregates, or which cause depolymerization, decrease the viscosity. A ten per cent solution of raw Para rubber in amyl acetate is fluid enough to filter through ordinary filter paper. Acetone is soluble in rubber to the extent of about 17 per cent. Rubber may be precipitated from benzene or ether solutions by the addition of alcohol or acetone. Tetrahydronaphthalene is said to have marked solvent power for rubber.

[157] Wilkinson, Neilson & Wylde, *J. Am. Chem. Soc.* *42*, 1377 (1920).
[158] *India Rubber J.* *46*, 723 (1913).
[159] *Gummi Ztg.* *27*, 1301 (1913).
[160] Kirchoff, *Caoutsch & gutta-percha* *12*, 8649 (1915).
[161] *India Rubber J.* *47*, 1054, 1093.

Liquid sulfur dioxide readily dissolves aromatic and unsaturated hydrocarbons but saturated non-benzenoid hydrocarbons are only very slightly soluble in this solvent. Edeleanu [162] has developed a refining method based upon these facts. The method has found greater favor in Europe than in America, although kerosene refined in this way has a lower specific gravity and usually better burning qualities than kerosene refined by sulfuric acid. The unsaturated and aromatic hydrocarbons are easily separated by distillation from the low boiling sulfur dioxide but the oils thus recovered have not yet proven to be of special industrial value. The fraction boiling at 150°–200° has been recommended as a turpentine substitute. With many oils the liquid sulfur dioxide method does not yield water-white oils, and in such cases refining with small proportions of sulfuric acid must be resorted to in order to get this result. The separation of the aromatic and unsaturated hydrocarbons from the paraffines is much more efficient at low temperatures, a temperature of about — 12°C being recommended. The method readily lends itself to analytical separations and has been checked by Egloff, Moore and Morrell.[163] Benzene, toluene, and xylenes and mesitylene are completely miscible with this solvent at — 10° and when using 33 and 66 per cent by volume of liquid sulfur dioxide at — 18° the pentane, hexane, octane, monane and decane fractions and gasolene from light Pennsylvania petroleum are practically insoluble. At — 10°, using the same proportions of solvent, these paraffines are soluble to the extent of about 1.8 per cent. Pennsylvania kerosene was found to be 3.6 per cent soluble at — 10°, using 66 per cent by volume of the solvent. Amylenes are completely miscible at — 10° and — 18°. Cyclohexane is insoluble at — 18° and 3 per cent soluble in an equal volume of sulfur dioxide at — 4.5°, and naphthenes of higher boiling-point, following the general order of solubility noted above, are less soluble than cyclohexane.

The Non-benzenoid Hydrocarbons and Colloid Phenomena.

A very large number of organic substances are much more sparingly soluble in petroleum ether than in ethyl ether or other organic solvents and this fact accounts for the wide employment of mixtures of petroleum ether and ethyl ether in recrystallizing organic substances in laboratory research work; the ethyl ether evaporates more rapidly

[162] German Pat. 216,459; *Petroleum 9,* 862 (1914); Engler & Ubbelohde, *Z. angew. Chem. 1913,* 177.
[163] *Met. & Chem. Eng. 18,* 396 (1918).

and the substance crystallizes from the solvent mixture as it becomes continually richer in petroleum ether. However, when a high degree of supersaturation is quickly brought about, as by pouring a warm one to two per cent solution of stearic acid in gasoline, into a solution of a little sodium ethylate in gasoline, the whole quickly sets to a jelly.

Numerous attempts have been made to prepare stable petroleum jellies, or "solidified petroleum." The sodium stearate jellies are not very firm and soon begin to exude oil, according to the well-known phenomenon of syneresis, common to all jellies of this type. Other more or less solid preparations of petroleum oils are really emulsions.[164] A high-melting wax is sometimes added to stiffen the jelly and one patentee adds about 15 per cent of turpentine in order to get a larger proportion of alkali stearate into solution when warm. Anther patentee prepares an emulsion with gelatin which is then hardened by formaldehyde.[165]

Calcium soaps, when dry, give clear solutions with mineral oils, gelatinizing on cooling. On stirring in water emulsification and stiffening of the grease results. Commercial greases frequently contain up to 22 per cent of calcium soaps.[166]

Colloids containing mostly soap and a little mineral oil are manufactured and known usually as naphtha soaps. The presence of free fatty acid or unsaponified fatty oil assists in preventing the separation of the petroleum oil.[167]

The solubility of soaps in mineral oils increases rapidly with increasing molecular weight of the fatty acid, but in light petroleum ether the lead soaps are very sparingly soluble, 100 cc. of the hydrocarbon dissolving 0.0528 g. lead heptoate, 0.221 g. lead myristate and 0.017 g. lead stearate.[168]

The subject of emulsions lies somewhat far afield from the subject matter and purpose of the present volume but anyone working with the non-benzenoid hydrocarbons is apt to be concerned with emulsions of various types and a limited number of examples will therefore be briefly mentioned. The theory of emulsions has been very

[164] Kuess, *J. Soc. Chem. Ind. 1906,* 1141. Ten parts of stearin are combined with 9 parts caustic soda in 18 parts of water and 100 parts of kerosene stirred in, melted at 105°-115° and the alkali soap converted into the more insoluble Al or Mg soaps by adding magnesium or aluminum sulfate.

[165] van der Heyden, *J. Soc. Chem. Ind. 1906,* 236. For a general review see Behrend, *Kunstoffe. 1914,* 356.

[166] Cf. Holde, *Z. Chem. Ind. Koll. 3,* 270 (1908).

[167] Brit. Pat. 2,137 (1911); *Chem. Abs. 6,* 2014 (1912); 8, 1026 (1914).

[168] Neave, *Analyst 37,* 399 (1912).

thoroughly reviewed by Bancroft.[169] The emulsifying power of fatty acid soaps, for mineral or other oils, is well known but the sulfonic acid derivatives of petroleum hydrocarbons or their alkali salts, also possess this property to a high degree. The removal of these sulfonic acids from the treated oil by washing first with water and then with alkali, without undue loss of hydrocarbon oils, is one of the arts of the petroleum refiner. One of the most troublesome difficulties encountered by the refiner is the emulsification of water in oil, and this is particularly liable to occur in the manufacture of highly refined water white oils of the so-called liquid paraffine type. Also, when water is added to a heavy lubricating oil containing a lime soap the water becomes dispersed *in* the oil and will change it to a grease. As pointed out by Bancroft, an emulsifying agent is a substance which goes into the interface and produces a film; if the adsorption of the emulsifying agent lowers the surface tension on the water side of the interface more than it does on the oil side, the interface will tend to curve so as to be convex on the water side, and we shall have a tendency to emulsify oil in water. If the adsorption of the emulsifying agent lowers the surface tension on the oil side of the interface more than it does on the water side, the interface will tend to curve so as to be concave on the water side, and we shall have a tendency to emulsify water in oil.

Pickering[170] has described experiments on the emulsification of kerosene in fungicidal and insecticidal sprays, the oil being emulsified with water and lime or basic copper sulfate. The oil globules in such an emulsion are probably prevented from coalescing by being enveloped in a pellicle consisting of particles of the solid much more minute than the globules themselves. "Apparently a precipitate consisting of any insoluble substance which is wetted more easily by water than by oil, if in a sufficiently fine state of division, will equally act as an emulsifier." Emulsions made with such an insoluble emulsifier are in every respect similar to those made with soap and the like. Quite recently emulsions of heavy, nearly non-volatile oils have been prepared in casein solutions: these solutions can then be dried by spraying in a vacuum and the result is a flour, each globule of oil being protected by a film of dried casein. Flours have been made in this way containing as much as 85 per cent of oil. Other emulsions can probably be dried in the same manner. Apparently no

[169] *J. Phys. Chem. 16,* 177, 345, 475, 739 (1912) ; *17,* 501 (1913).
[170] *J. Chem. Soc. 91,* 2001 (1907).

industrial applications of this process have as yet been made in the case of mineral oils.

Adsorption phenomena are of more than academic interest. The highly adsorptive charcoals, particularly coconut charcoal, activated by superheated steam, which were developed during the war for the manufacture of military gas masks, have proven to be highly efficient in selectively adsorbing the vapors of liquid hydrocarbons from natural gas.[171] Good "fifty minute" charcoal will adsorb ten to fifteen per cent of its own weight of gasoline vapors. The charcoal granules employed are about 8 to 14 mesh and when saturated with adsorbed hydrocarbons the latter are expelled by superheated steam at about 250°C.

The selective adsorption of coloring matter from vaseline and lubricating oils by fuller's earth has long been known. When unrefined black vaseline is filtered through warm fuller's earth the first product is a perfectly fluid oil and the successive portions which come through are progressively more and more viscous. This induced Day [172] to subject a crude petroleum to similar treatment and it was found that the first liquid to come through the column of fuller's earth consisted of light low boiling hydrocarbons. Day realized the significance of these facts and stated that in this way petroleum in passing through strata of clay and fine sand could be greatly altered; asphaltic matter, if originally present, could in this way be removed by adsorption resulting in light petroleum of the Pennsylvania type. His views were communicated to the Petroleum Congress held in Paris in 1900 and, shortly after, Engler [173] confirmed Day's experiments. The subject was further investigated by Gilpin and Cram,[174] who liberated the oil in different sections of the fuller's earth columns by the addition of water. They found that the lighter fractions showed less loss, on treating with concentrated sulfuric acid, than the heavier more viscous fractions which were more strongly adsorbed and they interpreted this to mean that *unsaturated* hydrocarbons were selectively adsorbed by the fuller's earth. This would indicate that the crude oil employed by them contained large proportions of unsaturated hydrocarbons, which is extremely improbable. As to whether or not unsaturated hydrocarbons are selectively adsorbed by fuller's earth has not definitely been shown.

[171] Burrell, Oberfell & Voress, *Chem. & Met. Eng.* *24*, 156 (1921).
[172] *Proc. Am. Phil. Soc.* *36*, 154 (1897).
[173] *Z. angew. chem.* *1901*, 889.
[174] *Am. Chem. J.* *40*, 495 (1908).

Continuing these investigations Gilpin and Bransky [175] pointed out that it is not necessary to assume a vegetable origin for petroleums of the light Pennsylvania type. The petroleum found in the Trenton limestone is supposed to have been derived from organic remains buried in this strata, as indicated by the abundance of fossil remains found in this limestone, and this supposition is supported by the relatively large proportions of sulfur and nitrogenous compounds in this oil. By filtration of oils such as the Ohio-Trenton, California and Texas petroleums through a bed of fuller's earth, oils very similar to light Pennsylvania petroleum can be obtained. Any sufficiently fine grained and porous material is capable of absorption, to a greater or less degree, just as in the case of fuller's earth. Beaumont, Texas, petroleum containing 1.75 per cent sulfur, on passing through a kaolin filter gave a fraction containing 0.70 per cent sulfur.[176] In a later paper Gilpin and Schneeberger [177] showed that sulfur and nitrogen derivatives were selectively adsorbed from a heavy petroleum from Kern County, California. By two filtrations of this oil they obtained the following:

	Sp. Gr.	*% Sulfur*
Crude oil	0.912	0.541
Fraction A (1)	0.857	0.06
" A (2)	0.8604	0.07
" A (3)	0.869	0.104
" B (1)	0.862	0.072
" B (2)	0.8771	0.09
" B (3)	0.8803	0.141

One filtration gave the following results with respect to nitrogen,

	Sp. Gr.	*% Nitrogen*
Crude oil	0.889	0.761
Fraction (1)	0.8264	0.08
" (2)	0.8421	0.116
" (3)	0.852	0.289
" (4)	0.8614	0.315
" (5)	0.8737	0.332

A similar filtration of another sample of California petroleum of Sp. Gr. 0.9118 and boiling over the range 105°–340° gave fractions varying from the lightest, Sp. Gr. 0.8325, boiling-point 160°–195° to a fraction Sp. Gr. 0.8984 and boiling-point 329°–340°.

[175] *Am. Chem. J. 44*, 251 (1910).
[176] Richardson & Wallace, *J. Soc. Chem. Ind. 1902.*
[177] *Am. Chem. J. 50*, 59 (1913).

Chapter XVII. Physiological and Related Properties

Odor: The physiology of odor is exceedingly obscure. However some generalizations can be made with reference to the relation between chemical constitution and odor. The odor of a substance appears to be a property of the *whole molecule*, but is greatly affected by the presence or absence of certain groups and also by the relative positions of different groups. Thus, the odor of the unsaturated ketones isomeric with α-ionone (q.v.) is markedly affected by each change in the position of the double bond in the ring and by the positions of the methyl group, with reference to the ketonic side chain. The marked difference in odor between isomeric normal, secondary and tertiary alcohols is well known.

Many of the saturated non-benzenoid hydrocarbons have faint but more or less characteristic, rather agreeable odors. Methane and ethane are, to most persons, entirely odorless but the pentanes and other comparatively volatile hydrocarbons have odors, and many hydrocarbons having the group $-C(CH_3)_3$ or $-CH(CH_3)_2$ have camphor like odors, as do the aliphatic tertiary alcohols. The light fraction from the petroleum of the Jennings-Louisiana field and the gasolene obtained from the natural gas of the Houma-Louisiana field contains saturated hydrocarbons whose odor closely resembles turpentine. Unsaturated hydrocarbons have somewhat more pronounced odors than the corresponding saturated hydrocarbons but still much less intense than alcohols, esters, ketones, aldehydes, etc. The offensive odor of unrefined gasolines, particularly when made by cracking processes, has erroneously been attributed to unsaturated hydrocarbons but the malodorous constituents in such oils are naphthenic acids and derivatives containing sulfur or nitrogen. The older idea is accounted for probably by the notion that refining by sulfuric acid consists merely, or essentially, in removing unsaturated hydrocarbons. Certain conjugated dienes, for example cyclohexadiene, and the light condensate obtained on compressing Pintsch gas containing cyclo-

hexadiene and probably cyclopentadiene, possess sharp pungent odors when strongly inhaled. Diallyl has an odor resembling horse-radish and the effect of the double bond in changing the odor of propyl alcohol and propionic aldehyde to the very sharp irritating odors of allyl alcohol and acrolein, is well known. These examples also illustrate the fact that odor is a property of the *whole molecule*, not a blend or composite odor of the constituent groups; thus the double bond in propylene is practically odorless, and propyl alcohol and propionic aldehyde are quite without the sharp irritating properties of acrolein and allyl alcohol.

Cyclic unsaturated hydrocarbons such as the terpenes and sesquiterpenes have sweet agreeable odors. Fresh turpentine or pure pinene is sweet and agreeable in odor and the irritating offensive odor of the stored or oxidized product is due to formic acid and other oxidation products. Ring closing has very little effect upon odor, as, for example, n.hexane and cyclohexane, secondary hexyl alcohol and cyclohexanol; when, however, the closing of the ring affects the constitution, as in the conversion of an aldehyde group to a hydroxyl group the change in odor is pronounced.

Intensity of odor can hardly bear any relation to chemical stability as we find stable borneol, having a strong pepper and camphor-like odor, and α-terpineol, which readily decomposes, has a very faint odor, and many other illustrations of this relation could be given. Also mercaptans are not appreciably different from alcohols in stability but their odors are beyond comparison. It should be noted, however, that we are probably handicapped, in attempting to make comparisons and generalizations, by the fact that we can know only what the human nose tells us, and this we can only very imperfectly describe or record.[1]

The subject of odor, while seldom mentioned in chemical texts and reviews, is given attention in these pages as it is a sense which is exceedingly useful to organic chemists. In many cases impurities can be detected with reasonable certainty by means of the nose when chemical tests fail or are not sufficiently delicate.

Physiological Action: Strictly speaking, the saturated hydrocarbons cannot be said to have any physiological properties, although inhalation of the vapors of the more volatile ones quickly produce drowsiness, followed by anesthesia, and, in extreme cases, death by

[1] Cf. Henning, "Der Geruch," Leipsig, 1916.

asphyxiation may result.[2] Workers in paraffine wax plants frequently develop skin sores which are supposed to be due to the closing of the skin pores by the wax. The value of soft flexible paraffine as a coating over burns is merely that of a non-irritant mechanical protection, protecting the tissue from the air, temperature changes, and giving the growing new tissue mechanical support. The saturated hydrocarbons are not attacked by oxidizing enzymes or other active body fluids and accordingly are entirely inert in the digestive tract.

Viscous, water-white, tasteless mineral oils are widely sold for pharmaceutical purposes, under a variety of names, i. e., *paraffinum liquidum, liquid petrolatum,* paraffine oil and many special trade names. As has been pointed out by Marcusson most oils of this class contain no paraffine whatever but consist, like lubricating oils from which they are in fact made by drastic refining, of cyclic hydrocarbons of the so-called naphthene or polynaphthene class, C_nH_{2n-2}, and C_nH_{2n-4}. Such an oil examined by Marcusson[3] had the specific gravity $\frac{20°}{4°}$ of 0.8827 and showed the following analysis,

	Found	*Calculated for $C_{20}H_{38}$*
Carbon	86.74%	86.33%
Hydrogen	13.43	13.67

The freezing test, by which small proportions of paraffine may separate, if present, *may* serve to differentiate between oils made from paraffine base crudes, and those made from paraffine-free oils such as Russian Baku, California or Gulf Coast crudes, but its presence is hardly to be condemned since if the paraffine does not separate at room temperatures, it certainly could not do so in the body. Bastedo[4] reports a clinical investigation of Russian and American oils and states that the choice between different oils of these types is an open one "to be determined by palatability, depending upon the degree to which the refinement has been carried out." Bastedo agrees with the original recommendation of Sir Arbuthnot Lane that oils for internal use should have a specific gravity of not less than 0.885, on account of low viscosity and leakage. Exposure to sunlight in loosely stoppered bottles will develop taste and odor in from 4 to 10 days and often serves to differentiate between the quality of oils of equal palatability when freshly prepared.[5] Various chemical tests have

[2] Fühner, *Biochem. Z. 115,* 235 (1921).
[3] *Chem. Ztg. 1913,* 550.
[4] *J. Am. Med. Assoc.* March 6, 1915, p. 808.
[5] Brooks, *J. Am. Med. Assoc. 65,* 24 (1916).

been proposed to determine quality, which are of more or less value in eliminating the personal equation involved in testing by taste and odor. Good oils on treating with concentrated sulfuric acid at room temperature will not be colored more than pale straw yellow in 5 minutes.

Unsaturated hydrocarbons, ethylene, propylene, butylene and the amylenes, act upon the nerve centers producing first excitement and then narcosis. Amylene was proposed as an anesthetic by Snow in 1856, but it was found to be dangerous, due to sudden failure of cardiac motion. Its use was condemned by the French Academy soon after its introduction. Gwathmy[6] notes two deaths in 238 administrations. The liquid unsaturated hydrocarbons are mildly irritating to the skin and mucous membranes. Taken internally unsaturated hydrocarbons cause severe gastric irritation and may even lead to convulsions and death. The higher aliphatic alcohols, such as secondary octyl alcohol, geraniol and the terpene alcohols, have distinct bactericidal values though less than the phenols. The sesquiterpene alcohol santalol is of value in treatment of gonorrhea but the value of borneol or its esters, cineol, menthol and the like in bronchial infections lies more in the stimulating effect of these substances on the mucous membranes than in their slight bactericidal properties. The use of essential oils in medicine is very ancient and though many of the prescriptions of the old herb doctors have given way to carefully prepared and standardized extracts or to new synthetic drugs, many essential oils are used in cosmetics, and a few have distinct medicinal values, as American worm-seed or oil of chenopodium, the active constituent of which is ascaridol (q.v.). In the treatment of persons suffering from hookworm, oil of chenopodium is more efficaceous than thymol; both are about equally effective in removing necators, but oil of chenopodium is much superior to thymol in removing the more resistant species of hookworm.[7] Essential oils containing the ketone thujone, for example, the volatile oils of thuja, tansy, sage and wormwood (*Artemisia absinthium*), produce characteristic disturbances of the central nervous system which, in the case of persons addicted to the drinking of the liqueur absinth, results in "râge tanacetique."

Considerable difference of opinion seems to exist regarding the physiological properties of *d,l.* and *d.l,* or synthetic camphor. In

[6] "Anesthesia," 698, New York, 1914.
[7] Report of Uncinariasis Comm. Rockefeller Inst., N. Y., 1920.

England a court found that synthetic camphor possessed properties identical with those of natural camphor (except optical rotation) and therefore ruled that its use in pharmaceutical preparations was permissible.[8] One observer[9] stated that he could detect no difference between the three kinds of camphor, by peritoneal injection, and later[10] reaffirmed that all three varieties are equally active. Leyden and Welden[11] treated frogs with chloral hydrate and reduced the heart beat to 7, after which the beat was raised to 20 by either natural *d.*camphor or lævo-camphor but state that synthetic camphor was without action on the heart. Perkin's epicamphor was found to have an action on the heart slightly less than natural camphor.[12] On the other hand, Tsakalotos[13] states that synthetic *d.l.*camphor has the same heart action, also using frogs, as natural camphor, which statement is also made by Lutz.[14] Edsall and Means[15] investigated the effect of natural *d.*camphor on respiratory metabolism but their results were so irregular that they were unable to draw any conclusion. Camphor vapor in concentrations of one to two parts per million in air is sufficient to effect the heart action markedly. [Heubner, *Z. ges. exp. Med.* I, 267 (1913).] Natural camphor has, however, a pronounced effect on the muscular respiratory system.[16] Heffter[17] states that there is no apparent reason for not using synthetic camphor in spirits of camphor but suggests that its use internally be not recommended until adequate clinical results are available.

Sassen[18] used cats and dogs in studying the physiological properties of natural and artificial camphor and states that with these animals no material difference could be noted in the physiological effects of the two camphors. For both natural and artificial camphor the fatal dose is 2 grams per 1 kilo weight of the animal. Doses of 0.025 to 0.05 gram per kilo weight, of either camphor caused a perceptible increase in the heart's activity.

The United States and German Pharmacopœias prescribe natural camphor. Bruni[19] states that *l.*camphor is about 13 times as toxic as natural *d.*camphor and Langgaard and Maass[20] state that the

[8] *Pharm. Zentr. 50,* 563 (1909).
[9] Joachimoglu, *Arch exp. Path. Pharm. 80,* 1 (1916).
[10] Joachimoglu, *ibid., 80,* 259, 282 (1917).
[11] *Arch. exp. Path. Pharm. 80,* 24 (1916).
[12] Bredt & Perkin, *J. Chem. Soc. 103,* 2182 (1913).
[13] *J. pharm. chim. 17,* 198 (1918).
[14] *Berl. klin. Wochenschr. 52,* 322 (1915).
[15] *Arch. Int. Med. 14,* 897 (1914).
[16] Tsakalotos, *J. pharm. chim.* (7) *15,* 19 (1917).
[17] *Chem. Abs. 9,* 1970 (1915).
[18] Schimmel & Co. Semi-Ann. Rep. *1910* (2), 170.
[19] *Gazz. chim. Ital. 38* (2), 1 (1908).
[20] *Therap. Monatsch. 20,* 573 (1907).

pharmacological actions of the two forms of camphor are different but in their paper reference is made to trials in the Charlottenburg hospital, of synthetic and natural camphor and no difference was noted between the two when used internally or externally. However, the use of synthetic camphor for internal use was not approved during the war by the German advisory committee on medical affairs. It is difficult to draw any definite conclusion from these contradictory findings other than that the experimental methods employed must, in many cases, have been exceedingly crude. Borneol produces physiological effects very similar to camphor but less pronounced, which would seem to indicate that the oxidation of borneol in the body is not rapid. The action of fenchone is very similar to that of camphor.[21] Camphoric acid has the same antiseptic properties as camphor, but is much less stimulating. Large doses can be tolerated without danger and it has been recommended for bronchial and lung infections, including pneumonia, but clinical results are not yet available. Monobromocamphor and the two known isomeric monochlorocamphors have properties not differing materially from camphor; these halogen derivatives are unusually stable. In the attempt to get the same physiological action of camphor more promptly by means of a more soluble substance, the physiological properties of oxycamphor, obtained by reduction of camphorquinone

$$C_8H_{14}<\begin{array}{l}CO\\|\\CO\end{array} \longrightarrow C_8H_{14}<\begin{array}{l}CHOH\\|\\CO\end{array}$$

was tried, but this substance was found to produce effects diametrically opposite from camphor; whereas camphor stimulates the central nervous system, oxycamphor depresses excitation of the respiratory center and is accordingly a rapidly acting drug in dyspnœa.[22] Aminocamphor and bornylamine retard the heart action. None of the numerous derivatives of camphor have been found to possess properties on the whole equal to camphor.

The anesthetic action of a large number of volatile chlorinated hydrocarbons has been described.[23] Ethyl chloride, butyl chloride and amyl chloride are said to be dangerous. Carbon tetrachloride is very slow in its action and gives a prolonged anesthesia in which the convulsive stage is apt to be of long duration and acute. It is also

[21] *Arch. exp. Path. Pharm. 50,* 199 (1903).
[22] Cf. Fränkel, Arzneimittel Synthese, Ed. 3, *1919*, p. 748.
[23] Cf. Gwathmey, Anesthesia, 1914; Fränkel, Arzneimittel Synthese, Ed. 3, 1919.

more toxic and irritating to the mucous membranes than chloroform. Of the many chlorine derivatives whose anesthetic action has been more or less carefully determined, methyl chloroform CH_3CCl_3, and dichloroethylene $CHCl = CHCl$, appear to be the most promising,[24] but none have been clearly shown to be as satisfactory as chloroform, although it is generally recognized that it would be desirable to discover a satisfactory anesthetic of the character of chloroform but which would not form the toxic product phosgene, to which many of the fatalities under chloroform anesthesia, have been attributed.

It is beyond the purpose of the present monograph to review the whole field of physiological action and chemical structure, and is also foreign to the author's experience in research. These selected notes are therefore included which seem to bear upon the general thesis of the present volume.

Diethyl ketone, $C_2H_5CO.C_2H_5$, has pronounced soporific properties and has been recommended[25] as an inhalation anesthetic but seems to possess no particular merit. Cyclopentanone, cyclohexanone and cycloheptanone also have pronounced sleep producing power.

Cyclohexylamine and n.hexylamine have practically identical effects upon the blood pressure[26] (normal hexylamine has the most pronounced effect of any of the normal primary amines).

That the physiological properties of comparatively simple derivatives of the aliphatic hydrocarbons are very imperfectly known has been strikingly demonstrated during the recent war when three of the war poisons of greatest value proved to be substances of this class. The physiological properties of only one of these was comparatively well known, i. e., phosgene. Trichloromethyl chloroformate and mustard gas [β,β-dichloroethyl sulfide] were very imperfectly known before the war. The latter substance is an excellent illustration of the fact that a substance may have a very mild, sweet, rather agreeable *odor* and yet be exceedingly irritating, this substance killing tissues with which it comes in contact and, within a few hours after exposure, develops most painful blisters. Halogen derivatives adjacent to a carbonyl group are exceedingly irritating to the eyes and mucous membranes, as illustrated by the lachrymatory "gases" trichloromethyl and monochloromethyl chloroformates, $Cl.CO_2CCl_3$ and $Cl.CO_2CH_2Cl$, acetone derivatives CH_3COCH_2Br, $CH_2Cl.COCH_2Cl$ and the like, bromoacetic ester $CH_2Br.CO_2C_2H_5$,

[24] Wittgenstein, *Arch. exp. Path. Pharm.* *83*, 235 (1918).
[25] *Ann. chim. farmac.* *1892*, 124, 225.
[26] Cf. Abelons & Bardier, *J. phys.* *1909*, 34.

bromo acetophenone $C_6H_5COCH_2Br$ and the like. A case of deep destruction of the tissues was described by Bogert[27] as a result of brominating in acetic anhydride. The tissues were killed nearly to the bone, under unbroken skin. This substance would seem to be more destructive to the deeper tissues than mustard gas but we have no data as to effective concentrations, or, in fact, the identity and nature of the toxic substance.

[27] *J. Am. Chem. Soc.* 29, 239 (1906).

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